JAN 29 1947

REGISTERED No. M 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXIV] *SECTION A* [No. 5

NOVEMBER, 1946

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

ON FLUCTUATIONS OF PRESSURE AND TEMPERATURE IN THE ATMOSPHERE*

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Received June 17, 1946

1. Introduction

In dealing with a fluid medium in motion such as the atmosphere, the properties of the medium not only differ from point to point at the same instant, but also undergo variations at the same point in course of time. If S is any physical property of the medium which we wish to study, then S is a function of the co-ordinates x, y, z and the time t.

$$S = f(x, y, z, t) \tag{1}$$

$$dS = \frac{\partial S}{\partial x} \cdot dx + \frac{\partial S}{\partial y} \cdot dy + \frac{\partial S}{\partial z} \cdot dz + \frac{\partial S}{\partial t} \cdot dt$$

$$\frac{dS}{dt} = \frac{\partial S}{\partial x} \cdot \frac{dx}{dt} + \frac{\partial S}{\partial y} \cdot \frac{dy}{dt} + \frac{\partial S}{\partial z} \cdot \frac{dz}{dt} + \frac{\partial S}{\partial t}$$

$$= \frac{\partial S}{\partial x} \cdot u + \frac{\partial S}{\partial y} \cdot v + \frac{\partial S}{\partial z} \cdot w + \frac{\partial S}{\partial t} \tag{2}$$

where u, v, w are the x, y, z components of the velocity of flow at the point under consideration. Or

$$\left(\frac{d}{dt}\right) S = \left(\frac{\partial}{\partial t} + u \frac{\partial}{\partial x} + v \frac{\partial}{\partial y} + w \frac{\partial}{\partial z}\right) S \tag{3}$$

$\frac{dS}{dt}$ is the time rate of change of the property S over a particular element of the medium and is known as the *individual* variation. $\frac{\partial S}{\partial t}$ is the time rate of change of the property S at the fixed point in the medium and is known as the *local* variation.

The hydrodynamical equivalent of the principle of conservation of mass is the *equation of continuity* which states that the rate of change of density at a point in the medium is equal to the net excess of inflow of mass over outflow per unit time considered over a small volume element around

* Presented at the Annual Session of the Indian Academy of Sciences, held at Udaipur, in December 1945.

that point, divided by the volume of the element. Mathematically this is expressed by the equation:

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)+\frac{\partial}{\partial z}(\rho w)=0, \tag{4}$$

where ρ is the density at the point under consideration. This can also be written as:

$$\frac{\partial \rho}{\partial t}+\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)=0 \tag{4a}$$

2. Atmospheric Pressure and its Variations

To a very high degree of accuracy, the pressure at a level h in the atmosphere is given by the weight per unit area of the mass of the atmosphere above the level in question.

$$p=\int_h^\infty g\,\rho\,dz \tag{5}$$

The *local* variation of pressure at the level h is therefore given by:

$$\frac{\partial p}{\partial t}=\int_h^\infty g\frac{\partial \rho}{\partial t}\cdot dz$$

Substituting for $\frac{\partial \rho}{\partial t}$ from (4) we get:

$$\frac{\partial p}{\partial t}=-\int_h^\infty g\left[\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)+\frac{\partial}{\partial z}(\rho w)\right]dz$$

$$=-\int_h^\infty g\left[\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)\right]dz+g(\rho w)_h \tag{6}$$

The integral on the right-hand side represents the rate of transport of mass above the level h due to horizontal motion (advection); the second term represents the rate of change of mass above the level h due to vertical motion. At the surface of the earth $w=0$, so that:

$$\frac{\partial p_0}{\partial t}=-\int_0^\infty g\left[\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)\right]dz. \tag{7}$$

This equation tells us that a change of surface pressure can only be brought about by horizontal advection of mass above the place of observation. On the other hand, equation (6) shows that a change of pressure at

a higher level in the atmosphere can occur even in the absence of horizontal advection of mass in the atmospheric air column under consideration.

3. Fluctuations of Temperature in the Atmosphere

(*a*) *General Case.*—If we consider an element of air in the atmosphere, the temperature of the element can undergo changes due to two causes, *viz.*, (1) due to direct addition of heat to or removal of heat from the element, and (2) due to external work done on the element or by the element consequent on the changes of atmospheric pressure. This is expressed by the well-known First Law of Thermodynamics:

$$dQ = dU + dW = c_p\, dT - ART\frac{dp}{p}$$

Hence

$$\frac{dQ}{dt} = c_p\frac{dT}{dt} - \frac{ART}{p}\cdot\frac{dp}{dt}$$

Or

$$\frac{dT}{dt} = \frac{1}{c_p}\frac{dQ}{dt} + \frac{AR}{c_p}\cdot\frac{T}{p}\cdot\frac{dp}{dt} \tag{8}$$

Since we can measure only *local* changes of pressure and temperature in the atmosphere, we transform (8) with the help of (3) and get:

$$\begin{aligned}\frac{\partial T}{\partial t} = \frac{1}{c_p}\frac{dQ}{dt} &+ u\left(\frac{AR}{c_p}\cdot\frac{T}{p}\cdot\frac{\partial p}{\partial x} - \frac{\partial T}{\partial x}\right)\\ &+ v\left(\frac{AR}{c_p}\cdot\frac{T}{p}\cdot\frac{\partial p}{\partial y} - \frac{\partial T}{\partial y}\right)\\ &+ w\left(\frac{AR}{c_p}\cdot\frac{T}{p}\cdot\frac{\partial p}{\partial z} - \frac{\partial T}{\partial z}\right)\\ &+ \frac{AR}{c_p}\cdot\frac{T}{p}\cdot\frac{\partial p}{\partial t}\end{aligned} \tag{9}$$

Now, if θ is the potential temperature of the element of air, we have:

$$\theta = T\left(\frac{P}{p}\right)^{\frac{AR}{c_p}}$$

Hence

$$\frac{d\theta}{\theta} = \frac{dT}{T} - \frac{AR}{c_p}\frac{dp}{p}$$

Or

$$d\theta = \frac{\theta}{T}\left(dT - \frac{AR}{c_p}\cdot\frac{T}{p}\cdot dp\right)$$

Substituting this relation in (9) we get:

$$\frac{\partial T}{\partial t} = \frac{1}{c_p}\frac{dQ}{dt} - \frac{T}{\theta}\left(u\frac{\partial \theta}{\partial x} + v\frac{\partial \theta}{\partial y} + w\frac{\partial \theta}{\partial z}\right) + \frac{AR}{c_p}\cdot\frac{T}{p}\cdot\frac{\partial p}{\partial t} \qquad (10)$$

The first term on the right-hand side of (9) or (10) represents the change of temperature resulting from direct addition of heat due to non-adiabatic processes such as radiation, condensation, etc. The second and third terms involving u and v represent the changes resulting from horizontal advection in a non-uniform pressure and temperature field. The fourth term involving w represents the adiabatic change of temperature due to vertical movements. Since $\frac{\partial p}{\partial z} = -g\rho$ and $\frac{Ag}{c_p} = \Gamma$ (dry adiabatic lapse-rate), this term can also be written as: $w(\beta - \Gamma)$, where $\beta = -\frac{\partial T}{\partial z}$ (prevailing lapse-rate in the atmosphere). The last term on the right-hand side of (9) and (10) represents the adiabatic heating or cooling effect due to local changes of pressure.

(*b*) *Particular Case.*—If the processes are strictly adiabatic, then $dQ = 0$; also, if the wind is geostrophic we have:

$$u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y} = 0. \qquad (11)$$

In this case, equation (9) reduces to:

$$\frac{\partial T}{\partial t} = \frac{AR}{c_p}\frac{T}{p}\frac{\partial p}{\partial t} - \left(u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y}\right) - w(\Gamma - \beta). \qquad (12)$$

Under geostrophic conditions, the relation between horizontal temperature gradient and the variation of wind with height is given by the well-known equations:

$$\left.\begin{aligned}\frac{\partial}{\partial z}\left(\frac{u}{T}\right) &= -\frac{g}{2\omega \sin\phi}\cdot\frac{1}{T^2}\frac{\partial T}{\partial y}\\ \frac{\partial}{\partial z}\left(\frac{v}{T}\right) &= \frac{g}{2\omega \sin\phi}\cdot\frac{1}{T^2}\cdot\frac{\partial T}{\partial x}\end{aligned}\right\} \qquad (13)$$

From this we have:

$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} = T^2\frac{2\omega \sin\phi}{g}\left[u\frac{\partial}{\partial z}\left(\frac{v}{T}\right) - v\frac{\partial}{\partial z}\left(\frac{u}{T}\right)\right]$$

$$= T.\frac{2\omega \sin\phi}{g}\left(u\frac{\partial v}{\partial z} - v\frac{\partial u}{\partial z}\right) \qquad (14)$$

If ψ is the angle between the direction of the horizontal wind vector and the x-axis then:

$$\tan\psi = \frac{v}{u}$$

Hence

$$\frac{\partial}{\partial z}(\tan \psi) = \sec^2 \psi \frac{\partial \psi}{\partial z} = \left(1 + \frac{v^2}{u^2}\right) \frac{\partial \psi}{\partial z}$$

$$\frac{\partial}{\partial z}\left(\frac{v}{u}\right) = \frac{1}{u^2}\left(u \frac{\partial v}{\partial z} - v \frac{\partial u}{\partial z}\right)$$

Or

$$u \frac{\partial v}{\partial z} - v \frac{\partial u}{\partial z} = (u^2 + v^2) \frac{\partial \psi}{\partial z}$$

$$= V_h^2 \cdot \frac{\partial \psi}{\partial z}, \tag{15}$$

where V_h is the scalar value of the horizontal wind vector. Substituting in (14) we get:

$$u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = T \cdot \frac{2\omega \sin \theta}{g} \cdot V_h^2 \cdot \frac{\partial \psi}{\partial z} \tag{16}$$

Substituting (16) in (12) and transposing the terms we have:

$$w(\Gamma - \beta) = \frac{AR}{c_p} \cdot \frac{T}{p} \cdot \frac{\partial p}{\partial t} - \frac{\partial T}{\partial t} - \frac{2\omega \sin \phi}{g} \cdot T \cdot V_h^2 \cdot \frac{\partial \psi}{\partial z} \tag{17}$$

Equation (17) enables us to calculate the vertical wind component at any level in the atmosphere if we know the rate of change of pressure and temperature at the point in question, the vertical variation of the horizontal wind vector as well as the prevailing lapse-rate. The assumptions involved are that: (i) all changes are adiabatic, and (ii) the wind is geostrophic.

4. Inter-Relation between Pressure and Temperature in the Atmosphere

The relation between pressure and temperature in the atmosphere is given by the well-known fundamental law of atmospheric statics:

$$dp = -g \rho \, dz = -g \frac{p}{RT} dz.$$

On integration this leads to the familiar barometric formula:

$$\log \frac{p}{p_0} = -\frac{g}{R} \int_0^z \frac{dz}{T} = -\frac{g}{R} \cdot \frac{z}{T_m}, \tag{18}$$

where T_m is the *mean* temperature of the air column from the surface where the pressure is p_0 to the level z where the pressure is p. If we differentiate (18) keeping z constant and treating p, p_0 and T_m as variables, we get the following relation connecting the variation of pressure at the surface and

at the level z with the change in the mean temperature of the column between those two levels:

$$\Delta p_0 = \Delta p \cdot \frac{p_0}{p} - \frac{gz}{RT_m^2} \cdot p_0 \cdot \Delta T_m. \qquad (19)$$

From (19) it follows that if $\Delta T_m = 0$, then $\Delta p_0 = \Delta p \cdot \frac{p_0}{p}$. That is, a small change of pressure at a higher level in the atmosphere would give rise to much larger changes in the surface pressure when the mean temperature of the air column remains unchanged. For instance, a change of pressure of 1 mb. at a level of 16 gms. where $p \simeq 100$ mbs. would bring about a change of nearly 10 mbs. in the surface pressure. In the case of an incompressible medium, a change of pressure at any level would produce the same change at all levels below it; however, in the case of the atmosphere when extra mass is added above the level z to produce an increase of pressure at that level, the column below z gets compressed and part of the extra mass added sinks below that level. Hence, in order to produce an increase of pressure of 1 mb. at 16 kms., additional mass equivalent to 10 mbs. has to be added above that level.

In (19) if p and z relate to the level of the tropopause, then it will be seen that the change in the surface pressure can be *interpreted* as resulting from:

(i) Change of pressure Δp at the level of the tropopause due to addition of mass in the stratosphere;

(ii) Change of mean temperature ΔT_m of the tropospheric air column. In meteorological literature (i) is sometimes designated as the *primary pressure wave*, and (ii) as the *secondary pressure wave*.

One of the striking results furnished by aerological ascents is that the day-to-day variations of pressure at all levels in the troposphere are of the same order of magnitude as that observed at the surface. From (19) it follows that such a result is possible only if the primary and secondary pressure waves are opposite in phase. In other words, a rise of pressure at a higher level should be accompanied by a rise of temperature in the air column below that level and *vice versa*. This result is strikingly borne out by the correlation coefficients worked out by W. H. Dines based on sounding balloon ascents over England which showed a correlation of 0·95 between the pressure at 9 kms. and the mean temperature of the air column below that level. Besides this, Dines also found the following high correlation coefficients:—

(i) 0·84 between the height of the tropopause and the pressure at 9 kms.;

(ii) 0·79 between the height of the tropopause and the mean temperature of the troposphere below 9 kms.

Similar results have been obtained by other investigators from observations over Europe, America and India.

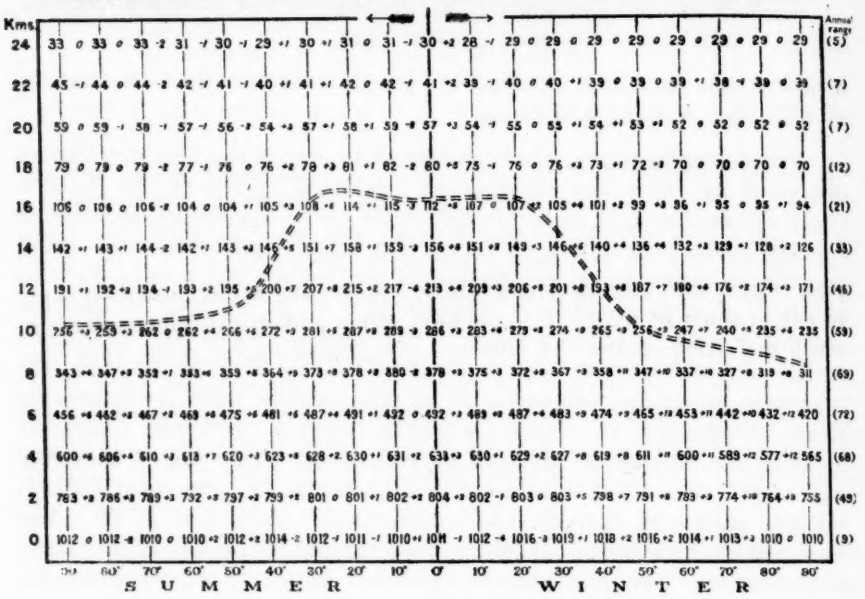
Various explanations have been offered to explain the high correlations discovered by Dines and subsequently confirmed by others. In the first instance it is clear that in an air column in static equilibrium, increase or decrease in the temperature of the column below a particular level would give rise to expansion or contraction of the column and consequently to transport of mass upwards or downwards through the level in question resulting in a rise or fall of pressure at that level so long as there is no horizontal convergence or divergence of mass. Again, if it be assumed that large-scale horizontal movements of air are possible from lower towards higher latitudes and *vice versa*, the high correlation coefficients discovered by Dines for middle latitudes can be understood. That such "***horizontal oscillations***" of the atmosphere are to be expected on theoretical grounds has been shown by Bjerknes and collaborators. According to the ideas developed by them, waves can be set up on the inclined surface of the tropopause over the temperate latitudes somewhat silimar to the waves on the polar front. The wave crests correspond to the pole-ward extension of tropical air with its high tropopause, while the wave troughs lie over regions where the polar air with its low tropopause has extended towards lower latitudes.

5. Distribution of Pressure over the Northern Hemisphere in Summer and in Winter and Effect of Meridional Advection

From the observed mean values of pressure at the surface and the mean temperature distribution in the atmosphere furnished from upper air soundings, it is possible to calculate the variation of pressure with height at various latitudes in summer and in winter. Such a calculation has been made by A. Wagner and the bold figures in Table I have been taken from his work. The pressure values in mms. given by Wagner have been converted into mbs. The figures in italics give the changes of pressure that would be produced *at the surface* at latitude ϕ if the entire atmospheric column above level h at latitude $\phi - 10°$ is bodily transported to the higher latitude by meridional advection.

TABLE I.

DISTRIBUTION OF PRESSURE OVER THE NORTHERN HEMISPHERE (MBS).



The table shows that the largest pressure gradients in the atmosphere occur in the middle and upper troposphere over polar and temperate latitudes in the winter months. When it is remembered that level for level temperatures decrease towards the north in the troposphere up to 9 or 10 kms., it is clear from the table that meridional advection from lower towards higher latitudes extending throughout the atmosphere will give rise to an increase of pressure at 9 kms. together with a rise in the mean temperature below that level. The table also shows that the annual range of pressure is largest in the middle and upper troposphere, while the range is comparatively small at the surface of the earth and also decreases rapidly in the stratosphere above 18 kms. It is interesting to see that within the tropics, horizontal advection cannot cause appreciable pressure variations especially in the summer months. It will also be seen from the table that while bodily displacement of the *entire* atmospheric column at a higher latitude by a similar column from a lower latitude does not cause large changes of surface pressure, similar replacement above levels of 4 to 10 kms. can produce large changes in the surface pressure. For instance, if the entire atmosphere above 40° N. is bodily shifted to 50° N. in winter,

there will be a rise of surface pressure of 2 mbs. only at the higher latitude. On the other hand, if the atmospheric column above 8 kms. at latitude 40° N. is transported to 50° N. without effecting any change in the atmosphere below 8 kms., there will be a rise of 11 mbs. in the surface pressure at latitude 50° N.

6. Pressure and Temperature Changes due to Advection

All changes of pressure and temperature in the atmosphere and consequently all weather phenomena are ultimately traceable to horizontal and vertical mass movements. These two movements are closely inter-linked with each other and we cannot hope to gain a correct or complete insight into atmospheric processes by confining our attention only to one or other of these. For instance, although vertical displacements in which the transformation of potential into kinetic energy takes place play a fundamental role in phenomena such as cyclones, thunderstorms, etc., we cannot ignore horizontal convergence or divergence with which these vertical movements are intimately bound up. Nevertheless, we can investigate the effect of purely horizontal mass movements and the changes which can result therefrom.

The problem of the fluctuations of pressure and temperature in the atmosphere brought about by horizontal advection has been discussed by a number of investigators among whom might be mentioned Hesselberg, Exner, Steiner, Hurwitz, Rossby, Ertel, Palmén and Refsdal. The problem can be stated as follows:—

Consider two atmospheric air columns A and B (*vide* Fig. 1) of unit cross-section extending upwards from the surface of the earth. The columns are in static equilibrium to start with, the distribution of pressure and temperature being different in the two columns. Horizontal advection now takes place from A towards B in one or more layers L_1, L_2, L_3,.... whereby the original air present in these layers in the column B is replaced by air of different density and temperature in the corresponding layers in column A. As a result of this, the column B, readjusts itself to a new position of equilibrium. If we have a sounding through the column B in the original state and also in the final state of equilibrium, we know the *local* changes of pressure and temperature. Is it possible to find out from the observed local changes the layer or layers in which advection has taken place and also the properties of the new samples of air brought in by advection? It is generally assumed for the sake of simplicity that all changes are adiabatic and that there is no lateral expansion or contraction of the column B as a result of the advection.

The simplest and clearest solution of the problem of calculating the local changes of pressure and temperature in an atmospheric air column *below* a certain level when addition or removal of mass takes place *above* the level in question was arrived at almost simultaneously but independently by Rossby and Steiner. Later, Rossby extended his theory to cover cases in which advection takes place in several layers of the column, and arrived at many interesting conclusions. A couple of years later (1930), Ertel discussed the same problem and arrived at the same results as Rossby. Some years after this (1935) Ertel and Sjan-zi-Li published a paper in which they claim to have discovered a " fundamental error " in Rossby's general advection theory and have worked out a new formula which they find gives more plausible results when applied to actual cases. This work

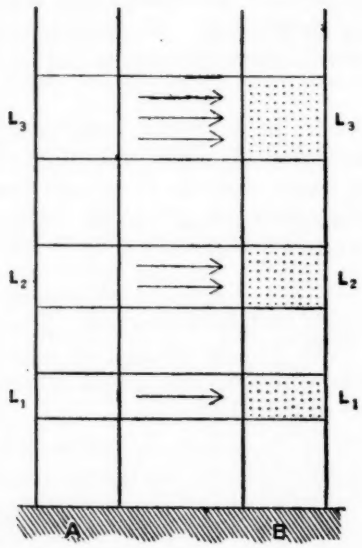


FIG. 1

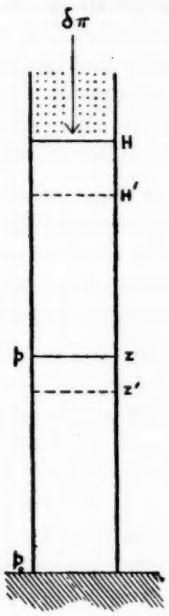


FIG. 2

has been quoted by Hurwitz in his recent book on " Dynamic Meteorology ". In view of the great importance of the subject, it was considered worth while to look into the matter afresh, especially the validity of the assumptions involved and the significance of the results obtained.

7. Effect of Addition or Removal of Mass at the Top of an Atmospheric Air Column

We start with the simplest case in which an addition of mass δM equivalent to an increase of pressure $\delta\pi = g\delta M$ takes place *above* the level H due to advection in an atmospheric air column of unit cross-section. What is the change of pressure and temperature at any fixed level z ($z < H$) in the column, it being assumed that there is no lateral expansion or contraction of the column from the surface to the level H ?

If the atmosphere were incompressible, it is clear that the pressure at every level would increase by $\delta\pi$. However, because of the compressibility of the air, the column from the surface to the level H gets compressed under the increased pressure, and occupies only a smaller height (volume) up to H′ in the new state of equilibrium. If we consider any fixed level z (Fig. 2), then the air which originally occupied the space from the surface to the level z occupies only the space up to z′ after compression under the increased pressure $\delta\pi$. If p_0 be the surface pressure and p the pressure at the level z before compression, then $p_0 - p$ is the weight of the air between these two levels. Since after compression this air occupies only the space up to z′ the pressure difference between the surface and z′ in the new state of equilibrium is also equal to $p_0 - p$. But the surface pressure in the new state of equilibrium is $p_0 + \delta\pi$. The pressure at the level z′ is therefore $p + \delta\pi$. Hence increase in pressure over the individual element of air at z which in the new state of equilibrium occupies the position z′ is $\delta\pi$. This is the *individual* change of pressure ($\delta_i p$). The change of pressure at the fixed level z is the *local* change ($\delta_l p$). The general relation connecting local and individual variations is given by equation (3) which in this case becomes:

$$\frac{dp}{dt} = u\frac{\partial p}{\partial x} + v\frac{\partial p}{\partial y} + w\frac{\partial p}{\partial z} + \frac{\partial p}{\partial t}$$

Since we assume that there is no lateral expansion or contraction of the column, $u = v = 0$. Also, $wdt = \delta z = z - z'$. Hence:

$$\delta_i p = \frac{\partial p}{\partial z} \cdot \delta z + \delta_l p$$

or:

$$\delta_l p = \delta_i p - \frac{\partial p}{\partial z} \cdot \delta z = \delta\pi - \frac{\partial p}{\partial z} \cdot \delta z \qquad (20)$$

Similarly the relation connecting the local and individual changes of temperature is:

$$\delta_l T = \delta_i T - \frac{\partial T}{\partial z} \cdot \delta z = \delta_i T + \beta \cdot \delta z \qquad (21$$

The evaluation of (20) and (21) depends upon the knowledge of the quantity δz which is the decrease in height (volume) of the column brought about by compression. In order to evaluate δz we have to make definite assumptions regarding the thermodynamics of the compression.

(*a*) *Isothermal Compression or Expansion.*—In this case, each element of air as it changes its level retains its original temperature. Let us now consider the column from the surface to the level z to be divided up into a number of thin elements $\Delta z_1, \Delta z_2, \ldots . \Delta z_n$. Consider the element of thickness Δz_r at the height z_r where the pressure is p_r. Since the compression is isothermal, we have:

$$p_r \cdot \Delta z_r = \text{constant}. \tag{22}$$

Hence the decrease in thickness (volume) of the element for an increase of pressure $\delta\pi$ is given by:

$$\delta (\Delta z_r) = - \delta\pi \cdot \frac{\Delta z_r}{p_r}$$

The decrease in thickness of the entire column is therefore given by:

$$\sum_1^n \delta (\Delta z_r) = \delta z = - \delta\pi \int_0^z \frac{dz}{p} \tag{23}$$

Hence:

$$\delta_l p = \delta\pi \left[1 + \frac{\partial p}{\partial z} \int_0^z \frac{dz}{p} \right] = \delta\pi \left[1 - g\rho \int_0^z \frac{dz}{p} \right] \tag{24}$$

And since in this case $\delta_i T = 0$, we have:

$$\delta_l T = - \beta \cdot \delta\pi \int_0^z \frac{dz}{p} \tag{25}$$

Since atmospheric movements conform more closely to adiabatic conditions, we shall now investigate this case.

(*b*) *Adiabatic Compression or Expansion.*—In this case we have to replace equation (22) by:

$$p_r \cdot (\Delta z_r)^\gamma = \text{constant} \tag{26}$$

Hence:

$$\delta (\Delta z_r) = - \frac{1}{\gamma} \cdot \delta\pi \frac{\Delta z_r}{p_r}$$

And so:

$$\sum_1^n \delta (\Delta z_r) = \delta z = - \frac{1}{\gamma} \cdot \delta\pi \int_0^z \frac{dz}{p} \tag{27}$$

We have therefore:

$$\delta_l p = \delta\pi \left[1 - \frac{g\rho}{\gamma} \int_0^z \frac{dz}{p}\right] = \delta\pi \left[1 - \frac{g}{R\gamma} \cdot \frac{p}{T} \int_0^z \frac{dz}{p}\right] \tag{28}$$

From equation (8), the individual change of temperature for an increase of pressure $\delta\pi$ under adiabatic conditions is given by:

$$\delta_i T = \frac{AR}{c_p} \cdot \frac{T}{p} \cdot \delta\pi$$

Hence:

$$\delta_l T = \frac{AR}{c_p} \cdot \frac{T}{p} \delta\pi - \frac{\beta}{\gamma} \delta\pi \int_0^z \frac{dz}{p}$$

$$= \frac{AR}{c_p} \cdot \frac{T}{p} \delta\pi \left[1 - \frac{\beta}{\Gamma} \frac{g}{R\gamma} \int_0^z \frac{dz}{p}\right] \tag{29}$$

From the hydrostatic equation, $dp = -g\rho dz$ we have:

$$\frac{dz}{p} = -\frac{1}{g\rho} \frac{dp}{p} = \frac{R}{g} T\, d\left(\frac{1}{p}\right)$$

Hence:

$$\int_0^z \frac{dz}{p} = \frac{R}{g} \int_{p_0}^{p} T\, d\left(\frac{1}{p}\right) = \frac{R}{g} T_m \left(\frac{1}{p} - \frac{1}{p_0}\right),$$

where T_m is the mean temperature of the column from the surface to the level z. (This is different from the mean temperature T_m in the barometric formula.)

Substituting this value of the integral in (28) and (29) we get:

$$\delta_l p = \delta\pi \left[1 - \frac{1}{\gamma} \cdot \frac{T_m}{T} \left(1 - \frac{p}{p_0}\right)\right] \tag{30}$$

$$\delta_l T = \delta\pi \cdot \frac{AR}{c_p} \cdot \frac{T}{p} \left[1 - \frac{\beta}{\Gamma} \cdot \frac{1}{\gamma} \cdot \frac{T_m}{T} \left(1 - \frac{p}{p_0}\right)\right]. \tag{31}$$

These expressions give the local variations of pressure and temperature at any level where the original pressure and temperature are p and T when the column is subjected to adiabatic compression under the influence of an advection current *above* the level in question, which causes an increase of pressure $\delta\pi$ at the ground level. The equations are valid only if the lower portion of the column retains its identity and there is no exchange of heat with the surroundings.

All the quantities in equations (30) and (31) are readily available from two consecutive aerological ascents over a station. If from the results of

two such ascents we calculate the values of $\delta\pi$ for a number of successive levels from the known values of p, T, T_m and $\delta_l p$, then these values should be very nearly constant if the observed change of surface pressure is due to advection at very high levels, and the lower atmosphere has not been appreciably disturbed in the interval between the two soundings. Such an example has been quoted by Rossby in which he has shown that a change of surface pressure by 19 mbs. at Trappes (France) between the 11th and 13th April 1912 was caused by advection above 12 kms.

(*c*) *Change of Lapse-Rate.*—We shall now derive an expression for the change of lapse-rate in the atmospheric air column subjected to an adiabatic compression $\delta\pi$ due to advection above the level H. Since the process is adiabatic, every individual element retains its potential temperature θ during its displacement from its original equilibrium position z where the pressure is p and temperature T to the new position z' where its pressure is $p+\delta\pi$ and temperature T'. Consider a thin layer of the column between z and $z+dz$, the corresponding potential temperatures being θ and $\theta+d\theta$. Then we have:

$$\frac{d\theta}{dz}=\frac{\theta}{\mathrm{T}}\left(\frac{d\mathrm{T}}{dz}-\frac{\mathrm{AR}}{c_p}\cdot\frac{\mathrm{T}}{p}\frac{dp}{dz}\right)=\frac{\theta}{\mathrm{T}}(\Gamma-\beta)$$

For the same element in the new position of equilibrium we have:

$$\frac{d\theta}{dz'}=\frac{\theta}{\mathrm{T}'}(\Gamma-\beta')$$

Hence:

$$\frac{\Gamma-\beta'}{\Gamma-\beta}=\frac{\mathrm{T}'}{\mathrm{T}}\cdot\frac{dz}{dz'}=\frac{p+\delta\pi}{p}=1+\frac{\delta\pi}{p}$$

Or:

$$\beta'=\beta-\frac{\delta\pi}{p}(\Gamma-\beta) \tag{32}$$

From this we see that: (i) if $\beta<\Gamma$ then $\beta'<\beta$; (ii) if $\beta>\Gamma$ then $\beta'>\beta$; (iii) if $\beta=\Gamma$ then $\beta'=\beta$. Thus, stable air becomes more stable and unstable air becomes more unstable by the addition of mass to the top of the column. If the air column is in neutral equilibrium, then there is no change in lapse-rate.

(*d*) *Atmosphere with Dry Adiabatic Lapse-Rate.*—Equations (30) and (31) assume a comparatively simple form if we consider an atmosphere with dry adiabatic lapse-rate. In this case the potential temperature θ is a constant at all levels, and the difference of temperature between the surface and any fixed level z is the same before and after the advection. Hence $(\delta_l \mathrm{T})_0=(\delta_l \mathrm{T})_z$; that is:

$$\frac{\mathrm{AR}}{c_p}\frac{\mathrm{T}_0}{p_0}\cdot\delta\pi=\frac{\mathrm{AR}}{c_p}\cdot\frac{\mathrm{T}}{p}\cdot\delta_l p$$

Hence:

$$\delta_l p = \frac{p}{p_0} \cdot \frac{T_0}{T} \cdot \delta\pi = \frac{p}{p_0} \cdot \left(\frac{p_0}{p}\right)^{\frac{AR}{c_p}} \cdot \delta\pi$$

$$= \delta\pi \left(\frac{p}{p_0}\right)^{\frac{1}{\gamma}} \tag{33}$$

$$\delta_l T = \frac{AR}{c_p} \cdot \frac{T_0}{p_0} \cdot \delta\pi = \frac{AR}{c_p} \cdot \frac{T}{p} \cdot \delta\pi \left(\frac{p}{p_0}\right)^{\frac{1}{\gamma}} \tag{34}$$

Table II gives the values of $\delta_l p$, $\delta_l T$, $\delta_i T$ and δz for an air column with dry adiabatic lapse-rate having a surface temperature of 300°A and surface pressure of 1,000 mbs. when an addition of mass equivalent to 10 mbs. takes place above the level of 12 gkms.

TABLE II

$\theta = T \cdot \left(\frac{1000}{p}\right)^{\frac{AR}{c_p}} = 300°A$; $p_0 = 1000$ mbs.; $\delta\pi = 10$ mbs.; $\beta = \Gamma = 10°C/gkm$

z (gkm)	T (Å)	p (mbs.)	$\left(\frac{p}{p_0}\right)^{1/\gamma}$	$\delta_l p = \delta\pi \cdot \left(\frac{p}{p_0}\right)^{1/\gamma}$ (mbs.)	$\delta_l T = \frac{AR}{C_p} \cdot \frac{T_0}{p_0} \cdot \delta\pi$ (°C.)	$\delta_i T = \frac{AR}{C_p} \cdot \frac{T}{p} \cdot \delta\pi$ (°C.)	$\delta z = -\frac{R}{g} \delta\pi \frac{T}{p}\left[1 - \left(\frac{p}{p_0}\right)^{1/\gamma}\right]$ (Metres)
0	300	1000	1·0000	10·0	0·86	0·86	0·0
1	290	890	0·9204	9·2	..	0·94	7·6
2	280	785	0·8414	8·4	..	1·03	16·7
3	270	692	0·7691	7·7	..	1·12	26·4
4	260	610	0·7025	7·0	..	1·23	37·3
5	250	532	0·6371	6·4	..	1·35	50·2
6	240	461	0·5754	5·8	..	1·50	64·9
7	230	398	0·5176	5·2	..	1·66	82·0
8	220	344	0·4667	4·7	..	1·84	100·3
9	210	289	0·4121	4·1	..	2·09	125·4
10	200	245	0·3664	3·7	..	2·35	152·1
11	190	206	0·3236	3·2	..	2·66	183·5
12	180	170	0·2830	2·8	..	3·06	223·0

(*e*) *Effect of Change of Cross-Section of the Air Column.*—Hitherto we have assumed that there is no lateral expansion or contraction of the column during its readjustment after the advection. We shall now investigate the case in which a change in the cross-section of the air column takes place with advective transport of mass aloft.

Consider an atmospheric air column of cross-section S. Let us assume that as a result of advection above the level H, the cross-section below the level z ($z < H$) changes to $S + \delta S$. In this case we have to replace equation (26) by:

$$p_r \cdot (S \Delta z_r)^\gamma = \text{constant}$$

The decrease in thickness of the element Δz_r for an increase in the external pressure by $\delta\pi$ is now given by the equation:

$$\frac{\delta\pi}{p_r} + \gamma \frac{\delta S}{S} + \gamma \frac{\delta(\Delta z_r)}{\Delta z_r} = 0$$

Hence:

$$\delta(\Delta z_r) = -\frac{1}{\gamma} \cdot \delta\pi \frac{\Delta z_r}{p_r} - (r-1)\, \Delta z_r,$$

where $r = 1 + \frac{\delta S}{S}$, is the relative increase in the cross-section of the element. The decrease in thickness of the entire column up to the level z is therefore given by:

$$\sum_1^n \delta(\Delta z_r) = \delta z^* = -\frac{1}{\gamma} \delta\pi \int_0^z \frac{dz}{p} - \int_0^z (r-1)\, dz$$

If r is constant at all levels below z this reduces to:

$$\delta z^* = -\frac{1}{\gamma} \delta\pi \int_0^z \frac{dz}{p} - (r-1)\, z \qquad (35)$$

Comparing (27) and (35) we see that δz^* is numerically greater than δz if $r > 1$. It follows, therefore, from equation (20) and (21) that the local changes of pressure and temperature are less than when there is no change in the cross-section of the column.

(*f*) *Pressure and Temperature Changes due to Advection in a Saturated Atmosphere.*—Hitherto we have assumed that the atmosphere is dry so that every individual element of air retains its potential temperature during its displacement from the original equilibrium position as a result of advection aloft. Let us now examine the case in which the atmosphere is saturated

either throughout its extent or in certain layers and condensation and evaporation of water take place during the displacement of the individual elements so that their changes of temperature follow the saturation adiabatic lapse-rate.

According to (27), when the atmosphere is dry, the decrease in thickness of the element Δz when the external pressure on the element is increased adiabatically from p to $p + \delta\pi$ is:

$$\delta(\Delta z) = -\frac{1}{\gamma} \cdot \delta\pi \frac{\Delta z}{p}.$$

The increase in temperature of the element as a result of the adiabatic compression is given by:

$$\delta T = \frac{AR}{c_p} \cdot \frac{T}{p} \cdot \delta\pi = \frac{R}{g} \cdot \frac{T}{p} \cdot \Gamma \cdot \delta\pi.$$

If the element of air remains saturated throughout the process, the increase in temperature of the element is given by:

$$\delta' T = \frac{R}{g} \cdot \frac{T}{p} \cdot \Gamma' \cdot \delta\pi,$$

where Γ' is the saturation adiabatic lapse-rate. Since $\Gamma' < \Gamma$ it follows that $\delta' T < \delta T$; that is, the increase in temperature of the element will be less in the second case. Hence in order to get the decrease in thickness of the element when the air remains saturated throughout the compression, we have to add to $\delta(\Delta z)$ the decrease in thickness of the element Δz as a result of the cooling under constant pressure by the amount $\delta T - \delta' T = \frac{R}{g} \cdot \frac{T}{p} \cdot \delta\pi (\Gamma - \Gamma')$. If we denote this additional contraction in thickness by $\delta'(\Delta z)$ we have:

$$\frac{\delta'(\Delta z)}{\Delta z} = \frac{\delta T - \delta' T}{T}$$

Or:

$$\delta'(\Delta z) = \frac{R}{g} \cdot \frac{\delta\pi}{p} \cdot (\Gamma - \Gamma')\, \Delta z$$

Hence the total decrease in thickness of the element Δz is given by:

$$\delta(\Delta z) + \delta'(\Delta z) = -\frac{1}{\gamma} \cdot \delta\pi \frac{\Delta z}{p} - \frac{R}{g} \cdot \delta\pi (\Gamma - \Gamma') \cdot \frac{\Delta z}{p}.$$

The total decrease in thickness of the column from the surface to the level z is therefore given by:

$$\delta z = -\frac{1}{\gamma} \delta\pi \int_0^z \frac{dz}{p} - \frac{R}{g} \delta\pi \int_0^z (\Gamma - \Gamma') \cdot \frac{dz}{p} \qquad (36)$$

The local changes of pressure and temperature can now be readily obtained by substituting this value of δz in equation (20) and (21). It will be seen that these changes are now less than in the case of the dry atmosphere.

8. Effect of Addition or Removal of Mass on the Pressure and Temperature above the Layer of Advection

(*a*) *Advection at the Surface.*—The simplest case is that in which addition of mass takes place at the surface. Let an advection current at the surface of the earth cause an increase of pressure $\delta\pi$ at the surface. It is assumed that the original atmospheric column is bodily lifted up by the advection current without individual pressure and temperature changes through a height δz (*vide* Fig. 3) given by:

$$\delta\pi = g\,\rho_a\,\delta z,$$

where ρ_a is the density of the advection current. The change of pressure at the fixed level z is then given by:

$$\delta_l p = -\frac{\partial p}{\partial z}\cdot\delta z = \frac{\rho}{\rho_a}\cdot\delta\pi \approx \frac{p}{p_0}\cdot\frac{T_a}{T}\cdot\delta\pi, \tag{37}$$

where T_a is the temperature of the new air mass brought in by advection. The local change of temperature is given by:

$$\delta_l T = -\frac{\partial T}{\partial z}\cdot\delta z = \frac{\beta}{g\,\rho_a}\cdot\delta\pi \approx \frac{R\,\beta}{g}\cdot\frac{T_a}{p_0}\cdot\delta\pi \tag{38}$$

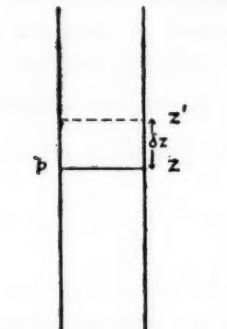


Fig. 3

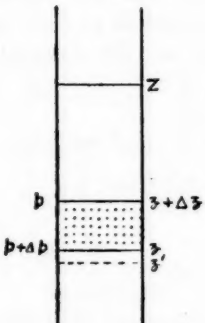


Fig. 4

(*b*) *Addition of Mass at any Arbitrary Level.*—We shall now consider the more general case in which the addition of mass takes place not at the surface but at some higher level. Let an addition of mass ΔM equivalent to an increase of pressure $\Delta\pi = g\Delta M$ take place between the levels z and $z + \Delta z$ in an atmospheric air column originally in static equilibrium. What is the local change of pressure and temperature at the level z $(z > z > 0)$?

In order to investigate this problem, let us imagine two weightless and frictionless discs in the column at z and $z + \Delta z$ which can be kept fixed or allowed to move up and down in the column as desired (*vide* Fig. 4). In the initial state, the discs are in equilibrium at z and $z + \Delta z$ respectively. Let $p + \Delta p$ and p be the pressures at z and $z + \Delta z$. Then:

$$\Delta p = g\rho\,\Delta z,$$

where ρ = density of the air between z and $z + \Delta z$.

Let us now imagine that the discs are kept fixed in position and the air between them replaced by a new sample of air of density ρ_a.
We then have:

$$\Delta p_a = g \cdot \rho_a\,\Delta z = \Delta p + \Delta\pi.$$

Let the discs be now released so that the column readjusts itself to its new position of equilibrium. What will be the new positions of the discs z and $z + \Delta z$?

The pressure on the lower surface of the disc z is $p + \Delta p$ and on its upper surface, $p + \Delta p_a = p + \Delta p + \Delta\pi$. The disc z and the column above it will therefore move down bodily compressing adiabatically the atmospheric column below it until equality of pressures is established on the two sides of the disc in its new position of equilibrium z'. The distance $z - z' = \delta a$ is given by:

$$\delta a = -\frac{1}{\gamma} \cdot \Delta\pi \int_0^z \frac{dz}{p}. \tag{39}$$

Let us now consider the equilibrium position of the disc $z + \Delta z$. The pressure on its upper surface is p and on its lower surface is p_a where p_a is the pressure of the new sample of air introduced between z and $z + \Delta z$. We may now distinguish between two cases.

(1) If $p_a = p$, then the disc $z + \Delta z$ will be at the same distance from the disc z in the new position of equilibrium. In this case, therefore, the entire column above the disc z will sink *bodily* through the distance δa. The

individual changes of pressure and temperature of any element above the layer of advection are zero, while the *local* changes are given by:

$$\left.\begin{aligned} \delta_l p &= -\frac{\partial p}{\partial z} \cdot \delta a \\ \delta_l \mathrm{T} &= -\frac{\partial \mathrm{T}}{\partial z} \cdot \delta a \end{aligned}\right\} \tag{40}$$

We see that when $\Delta\pi$ is positive, $\delta_l p$ and $\delta_l \mathrm{T}$ are both negative. That is, when a stratum of air in an atmospheric air column is displaced by another stratum of the same thickness but greater mass, there is an *increase* of pressure at every level *below* the layer of advection, and a *decrease* of pressure at every level *above*, provided the pressure at the upper boundary of the advection layer remains constant during the displacement.

(2) Let us now consider the case in which p_a is not equal to p. The air between z and $z + \Delta z$ will then undergo adiabatic expansion if $p_a > p$ or compression if $p_a < p$, until p_a becomes equal to p. In this process the column of air above $z + \Delta z$ will move bodily up or down without individual changes of pressure and temperature. Let:

$$\begin{aligned} p_a - p &= \delta_a p \\ \rho_a - \rho &= \delta_a \rho \\ \mathrm{T}_a - \mathrm{T} &= \delta_a \mathrm{T} \end{aligned}$$

If $p_a > p$, then the increase in Δz during the adiabatic expansion from p_a to p is given by:

$$\delta\beta = \frac{1}{\gamma} \cdot \delta_a p \cdot \frac{\Delta z}{p} \tag{41}$$

Now, we have:

$$\delta_a p = \mathrm{R}\,(\mathrm{T} \cdot \delta_a \rho + \rho \cdot \delta_a \mathrm{T}) \tag{42}$$

$$\Delta\pi = g\,(\rho_a - \rho) \cdot \Delta z = g \cdot \delta_a \rho \cdot \Delta z$$

Or:
$$\delta_a \rho = \frac{1}{g} \cdot \frac{\Delta\pi}{\Delta z} = -\frac{1}{g} \cdot \frac{d\pi}{dz},$$

where π is the total increase in mass above the level z due to advection in the entire column above this level.

Hence:

$$\delta_a p = \mathrm{R}\left(-\frac{1}{g} \cdot \frac{d\pi}{dz} \cdot \mathrm{T} + \rho\, \delta_a \mathrm{T}\right) \tag{43}$$

Therefore:

$$\delta\beta = -\frac{\mathrm{R}}{g\gamma} \cdot \frac{\mathrm{T}}{p} \cdot \frac{d\pi}{dz} \cdot \Delta z + \frac{1}{\gamma} \cdot \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot \Delta z \tag{44}$$

The resultant downward displacement of the individual layer at z due to adiabatic compression of the column below z and adiabatic expansion as the stratum between z and $z + \Delta z$ is given by:

$$\delta z = \delta\alpha + \delta\beta$$

The local changes of pressure and temperature are given by:

$$\left.\begin{aligned} \delta_l p &= -\frac{\partial p}{\partial z} \cdot \delta z \\ \delta_l T &= -\frac{\partial T}{\partial z} \cdot \delta z \end{aligned}\right\} \qquad (45)$$

It will be seen that when $\delta_a p = 0$, $\delta z = \delta\alpha$, so that (40) and (45) become identical. In this case we see from (42) that:

$$\delta_a \rho = \rho \cdot \frac{\delta_a T}{T}.$$

This means that the change of mass of the air between z and $z + \Delta z$ is brought about entirely by a change in temperature of the air at constant pressure.

If $\Delta\pi$ is positive and $\delta_a p$ is also positive, we see from (39) and (41) that $\delta\alpha$ and $\delta\beta$ are opposite in sign. In particular, if $\delta\alpha$ and $\delta\beta$ are numerically equal, then $\delta z = 0$; that is, there is no displacement of the individual element of air at z. In this special case, therefore, the local changes of pressure and temperature at any point above the layer of advection are zero. The upward displacement of the disc $z + \Delta z$ and the column above it due to the adiabatic expansion of the stratum is exactly equal in magnitude to the downward displacement of the disc z and the whole column above it due to adiabatic compression of the column below z. In the final state of equilibrium, the disc z is displaced to z' while the disc $z + \Delta z$ and the column above it remain undisturbed.

9. Advection in Several Layers of an Air Column

We shall now consider the case in which the atmospheric air column is traversed by arbitrary advection currents so that displacements and replacements of air take place in several layers throughout the length of the column.

In this case (*vide* Fig. 5) if we consider any individual element of air in the column at a height z above the ground, then changes of mass take place both above and below this level. The final displacement of the individual element at z is the resultant of:

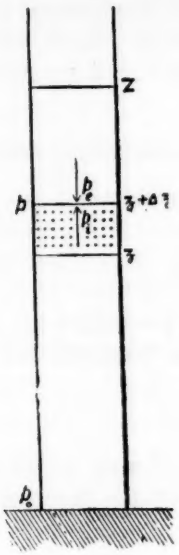


FIG. 5

(1) Adiabatic compression or expansion of the individual elements in the column below z due to the change in the external pressure p_e to which the individual elements in the column are subjected as a result of advection in the entire column above the element in question;

(2) Adiabatic compression or expansion of the individual elements in the column below z due to the change in the internal pressure p_i as a result of advection in the individual elements.

Imagine the column from the surface to the level z to be divided up into a number of thin elements $\Delta z_1, \Delta z_2, \ldots \Delta z_n$. Let $\delta_a\rho_1, \delta_a\rho_2, \ldots \delta_a\rho_n$ denote the change in density in the individual elements as a result of advection; $\delta_a p_1, \delta_a p_2, \ldots \delta_a p_n$ and $\delta_a T_1, \delta_a T_2, \ldots \delta_a T_n$, the corresponding changes of pressure and temperature.

The total increase of pressure over the individual element at z as a result of advection aloft is given by:

$$\pi(z) = \int_z^\infty g \cdot \delta_a \rho \cdot dz$$

The decrease in thickness of the element Δz as a result of the adiabatic increase of pressure from p to $p + \pi(z)$ is given by:

$$\delta(\Delta z) = -\frac{1}{\gamma} \cdot \pi(z) \frac{\Delta z}{p}.$$

The decrease in height of the column from the surface to the level z is therefore given by:

$$\alpha = \sum_{1}^{n} -\frac{1}{\gamma} \cdot \pi(z_r) \frac{\Delta z_r}{p_r} = -\frac{1}{\gamma} \int_0^z \pi \frac{dz}{p}. \tag{46}$$

From (41) and (44), we see that the total increase in height of the column from the surface to the level z as a result of adiabatic expansion of the individual elements due to the change in the internal pressures is given by:

$$\beta = \sum_{1}^{n} \frac{1}{\gamma} \cdot \delta_a p_r \cdot \frac{\Delta z_r}{p_r} = \frac{1}{\gamma} \int_0^z \delta_a p \frac{dz}{p}$$

$$= \frac{1}{\gamma} \int_0^z \mathrm{R} \left(-\frac{1}{g} \frac{d\pi}{dz} \cdot \mathrm{T} + \rho \cdot \delta_a \mathrm{T} \right) \frac{dz}{p} \tag{47}$$

Hence, the resultant downward displacement of the irdividual layer at z is given by:

$$\delta z = \alpha + \beta = -\frac{1}{\gamma} \int_0^z \pi \frac{dz}{p} - \frac{\mathrm{R}}{g\gamma} \int_0^z \frac{\mathrm{T}}{p} \frac{d\pi}{dz} \cdot dz + \frac{1}{\gamma} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} dz$$

$$= -\frac{1}{\gamma} \int_0^z \pi \frac{dz}{p} - \frac{\mathrm{R}}{g\gamma} \cdot \left[\pi \cdot \frac{\mathrm{T}}{p} \right]_0^z + \frac{\mathrm{R}}{g\gamma} \int_0^z \pi \left(\frac{1}{p} \cdot \frac{\partial \mathrm{T}}{\partial z} - \frac{\mathrm{T}}{p^2} \frac{\partial p}{\partial z} \right) dz$$

$$+ \frac{1}{\gamma} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot dz$$

$$= -\frac{1}{\gamma} \int_0^z \pi \frac{dz}{p} - \frac{\mathrm{R}}{g\gamma} \left(\frac{\pi \mathrm{T}}{p} - \frac{\pi_0 \mathrm{T}_0}{p_0} \right) + \frac{\mathrm{R}}{g\gamma} \cdot \int_0^z \frac{\pi}{p} \cdot \frac{\partial \mathrm{T}}{\partial z} \cdot dz$$

$$+ \frac{1}{\gamma} \int_0^z \pi \cdot \frac{dz}{p} + \frac{1}{\gamma} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot dz$$

$$= \frac{\mathrm{R}}{g\gamma} \left(\frac{\pi_0 \mathrm{T}_0}{p_0} - \frac{\pi \mathrm{T}}{p} \right) + \frac{\mathrm{R}}{g\gamma} \int_0^z \frac{\pi}{p} \cdot \frac{\partial \mathrm{T}}{\partial z} \cdot dz + \frac{1}{\gamma} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot dz$$

where π_0, p_0, T_0 are the values of π, p, T at the surface.

The local variation of pressure at the level z is therefore given by:

$$\delta_l p = \pi - \frac{\partial p}{\partial z} \cdot \delta z = \pi + g\rho\, \delta z = \pi + \frac{g}{\mathrm{R}} \cdot \frac{p}{\mathrm{T}} \cdot \delta z$$

$$= \pi \left(1 - \frac{1}{\gamma}\right) + \left(\frac{1}{\gamma} \cdot \frac{\pi_0 \mathrm{T}_0}{p_0}\right) \cdot \frac{p}{\mathrm{T}} + \frac{1}{\gamma} \cdot \frac{p}{\mathrm{T}} \int_0^z \frac{\pi}{p} \cdot \frac{\partial \mathrm{T}}{\partial z} \cdot dz$$

$$+ \frac{g}{\mathrm{R}\gamma} \cdot \frac{p}{\mathrm{T}} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot dz \tag{48}$$

Let $$\phi = \int_0^z \frac{\pi}{p} \cdot \frac{\partial \mathrm{T}}{\partial z} \cdot dz; \tag{49}$$

Then $$\frac{d\phi}{dz} = \frac{\pi}{p} \cdot \frac{\partial \mathrm{T}}{\partial z} = -\frac{\pi}{p} \cdot \beta$$

Hence $$\pi = -\frac{p}{\beta} \cdot \frac{d\phi}{dz} \tag{50}$$

Substituting (49) and (50) in (48) and simplifying we get:

$$\frac{d\phi}{dz} - \frac{1}{\gamma - 1} \cdot \frac{\beta}{\mathrm{T}} \cdot \phi$$

$$= \frac{1}{\gamma - 1} \cdot \left[\frac{\beta}{\mathrm{T}} \cdot \frac{\pi_0 \mathrm{T}_0}{p_0} + \frac{\beta}{\mathrm{T}} \cdot \frac{g}{\mathrm{R}} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot dz - \gamma \cdot \frac{\beta}{\mathrm{T}} \cdot \delta_l p\right]$$

Let $\frac{\mathrm{I}}{\gamma - 1} = \mathrm{P}$; $\frac{\pi_0 \mathrm{T}_0}{p_0} = \mathrm{Q}$; and $\frac{g}{\mathrm{R}} \int_0^z \frac{\delta_a \mathrm{T}}{\mathrm{T}} \cdot dz = \mathrm{S}$

Then, we have:

$$\frac{d\phi}{dz} + \mathrm{P}\, \frac{d}{dz} (\log \mathrm{T}) \cdot \phi = \mathrm{P}\left[\frac{\beta}{\mathrm{T}} \cdot (\mathrm{Q} + \mathrm{S}) - \gamma \cdot \frac{\beta}{p} \cdot \delta_l p\right] \tag{51}$$

Solving this equation for ϕ we get:

$$\phi = e^{-\mathrm{P}\int_0^z \frac{d}{dz}(\log \mathrm{T})\, dz} \left[\int_0^z e^{\mathrm{P}\int_0^z \frac{d}{dz}(\log \mathrm{T})\, dz} \cdot \mathrm{P}\left\{\frac{\beta}{\mathrm{T}} (\mathrm{Q} + \mathrm{S}) - \gamma \cdot \frac{\beta}{\gamma}\, \delta_l p\right\} dz\right]$$

$$= \left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{-\mathrm{P}} \left[\int_0^z \left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\mathrm{P}} \cdot \mathrm{P}\left\{\frac{\beta}{\mathrm{T}} (\mathrm{Q} + \mathrm{S}) - \gamma \cdot \frac{\beta}{p} \cdot \delta_l p\right\} dz\right] \tag{52}$$

Hence:

$$\frac{d\phi}{dz} = -\beta \cdot \frac{\pi}{p}$$

$$= \mathrm{P}\left\{\frac{\beta}{\mathrm{T}}(\mathrm{Q}+\mathrm{S}) - \gamma \cdot \frac{\beta}{p} \cdot \delta_l p\right\} - \mathrm{P} \cdot \left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{-\mathrm{P}-1} \cdot \frac{1}{\mathrm{T}_0} \cdot \frac{\partial \mathrm{T}}{\partial z}$$

$$\left[\int_0^z \left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\mathrm{P}} \cdot \mathrm{P}\left\{\frac{\beta}{\mathrm{T}}(\mathrm{Q}+\mathrm{S}) - \gamma \cdot \frac{\beta}{p} \cdot \delta_l p\right\} dz\right]$$

Therefore:

$$\pi = -\frac{p}{\beta} \cdot \mathrm{P}\left\{\frac{\beta}{\mathrm{T}}(\mathrm{Q}+\mathrm{S}) - \gamma \cdot \frac{\beta}{p} \cdot \delta_l p\right\}$$

$$-\frac{p}{\beta} \cdot \mathrm{P}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{-(\mathrm{P}+1)} \cdot \frac{1}{\mathrm{T}_0} \cdot \beta \left[\int_0^z \left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\mathrm{P}} \cdot \mathrm{P}\left\{\frac{\beta}{\mathrm{T}}(\mathrm{Q}+\mathrm{S}) - \gamma \cdot \frac{\beta}{p}\delta_l p\right\} dz\right]$$

$$= -\mathrm{P}(\mathrm{Q}+\mathrm{S}) \cdot \frac{p}{\mathrm{T}} + \mathrm{P} \cdot \gamma \cdot \delta_l p$$

$$+ \mathrm{P}^2(\mathrm{Q}+\mathrm{S}) \frac{p}{\mathrm{T}^{\mathrm{P}+1}} \int_0^z \frac{1}{p} \frac{d}{dz}(\mathrm{T}^{\mathrm{P}})\, dz$$

$$- \mathrm{P}^2 \gamma \frac{p}{\mathrm{T}^{\mathrm{P}+1}} \int_0^z \frac{\delta_l p}{p} \cdot \frac{1}{\mathrm{P}+1} \frac{d}{dz}(\mathrm{T}^{\mathrm{P}+1})\, dz$$

$$= -\mathrm{P}(\mathrm{Q}+\mathrm{S}) \frac{p}{\mathrm{T}} + \mathrm{P} \cdot \gamma \cdot \delta_l p$$

$$+ \mathrm{P}(\mathrm{Q}+\mathrm{S}) \frac{p}{\mathrm{T}^{\mathrm{P}+1}} (\mathrm{T}^{\mathrm{P}} - \mathrm{T}_0{}^{\mathrm{P}})$$

$$- \mathrm{P}^2 \gamma \frac{p}{\mathrm{T}^{\mathrm{P}+1}} \frac{1}{\mathrm{P}+1} \int_0^z \frac{\delta_l p}{p} \cdot \frac{d}{dz}(\mathrm{T}^{\mathrm{P}+1})\, dz$$

$$\pi = \mathrm{P} \cdot \gamma \cdot \delta_l p - \mathrm{P}(\mathrm{Q}+\mathrm{S}) \frac{p}{\mathrm{T}} \cdot \left(\frac{\mathrm{T}_0}{\mathrm{T}}\right)^{\mathrm{P}} - \mathrm{P} \frac{p}{\mathrm{T}^{\mathrm{P}+1}} \int_0^z \left(\frac{\delta_l p}{p}\right) \cdot \frac{d}{dz}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\mathrm{P}+1} \cdot dz$$

$$= \mathrm{P}\left[\gamma \cdot \delta_l p - (\mathrm{Q}+\mathrm{S}) \cdot \frac{p}{\mathrm{T}_0}\left(\frac{\mathrm{T}_0}{\mathrm{T}}\right)^{\mathrm{P}+1} - p \cdot \left(\frac{\mathrm{T}_0}{\mathrm{T}}\right)^{\mathrm{P}+1} \cdot \right.$$

$$\left. \int_0^z \left(\frac{\delta_l p}{p}\right) \cdot \frac{d}{dz}\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\mathrm{P}+1} dz\right]$$

$$= \frac{\gamma}{\gamma-1}\,\delta_l p - \frac{1}{\gamma-1}\,p\cdot\left(\frac{T_0}{T}\right)^{\frac{\gamma}{\gamma-1}}\left[\frac{\pi_0}{p_0}+\frac{g}{R\,T_0}\int_0^z \frac{\delta_a T}{T}\cdot dz\right.$$

$$\left. + \int_0^z \left(\frac{\delta_l p}{p}\right)\cdot\frac{d}{dz}\left(\frac{T}{T_0}\right)^{\frac{\gamma}{\gamma-1}}\cdot dz\right]$$

Since:

$$\frac{\gamma}{\gamma-1}=\frac{1\cdot4}{0\cdot4}=3\cdot5;\quad \frac{1}{\gamma-1}=\frac{1}{0\cdot4}=2\cdot5,$$

We have:

$$\pi = 3\cdot5\,\delta_l p - 2\cdot5\,p\left(\frac{T_0}{T}\right)^{3\cdot5}\left[\frac{\pi_0}{p_0}+\frac{g}{R\,T_0}\int_0^z \frac{\delta_a T}{T}\cdot dz\right.$$

$$\left. + \int_0^z \left(\frac{\delta_l p}{p}\right)\cdot\frac{d}{dz}\left(\frac{T}{T_0}\right)^{3\cdot5} dz\right]$$

$$= 3\cdot5\,\delta_l p - 2\cdot5\,p\left(\frac{T_0}{T}\right)^{3\cdot5}\left[\frac{\pi_0}{p_0}+\frac{g}{R\,T_0}\int_0^z \frac{\delta_a T}{T}\cdot dz\right.$$

$$\left. + \frac{\delta_l p}{p}\cdot\left(\frac{T}{T_0}\right)^{3\cdot5} - \frac{\pi_0}{p_0} - \int_0^z \left(\frac{T}{T_0}\right)^{3\cdot5}\frac{d}{dz}\left(\frac{\delta_l p}{p}\right) dz\right]$$

$$= \delta_l p - 2\cdot5\,p\left(\frac{T_0}{T}\right)^{3\cdot5}\left[\frac{g}{R\,T_0}\int_0^z \frac{\delta_a T}{T}\,dz - \int_0^z \left(\frac{T}{T_0}\right)^{3\cdot5}\frac{d}{dz}\left(\frac{\delta_l p}{p}\right) dz\right] \qquad (53)$$

10. General Advection Theory of Rossby

The expression for π developed in the preceding section assumes a comparative form if we make special assumptions regarding the nature of the advection currents in the atmospheric column.

Rossby assumed that at any height z the layer of thickness dz is displaced by another layer of the same thickness and that *the pressure at the upper boundary of the advection layer remains constant during the displacement.* This means that in equation (47) $\delta_a p_1$, $\delta_a p_2$, ... are each equal to zero so that $\beta = 0$. Hence:

$$\delta z = \alpha = -\frac{1}{\gamma}\int_0^z \pi\,\frac{dz}{p}$$

The *local* change of pressure at the level z is therefore given by :

$$\delta_l p = \pi - \frac{\partial p}{\partial z} \cdot \delta z = \pi - \frac{g}{R\gamma} \cdot \frac{p}{T} \int_0^z \pi \frac{dz}{p}$$

As has been shown by Rossby, this equation when solved for π gives:

$$\pi = \delta_l p + \frac{g}{R\gamma} \cdot \frac{1}{\theta} \int_0^z \delta_l p \cdot \frac{\theta}{T} \cdot dz \qquad (54)$$

where θ is the potential temperature at the level z.

It will be clear from the considerations in Section 8 that Rossby's assumption essentially means that the result of addition of mass due to advection in the atmospheric air column *below* any arbitrary level z is to produce a *bodily sinking* of the entire column above this level through a distance equal to the adiabatic compression of the column from the surface to the level z. The thickness of an individual element Δz remains unchanged as a result of advection within the element, but the entire column below the element is adiabatically compressed by an amount $\delta\alpha$ given by equation (39). We thus see that *Rossby's assumption leads to the result that there is a local decrease of pressure* ($\delta_l p$ *negative*) *at all levels above the layers influenced by advection.* Indeed, practically all the results derived and discussed by Rossby in the latter part of his paper are a direct outcome of this assumption.

With the assumptions made by Rossby, it is also possible to derive an expression for the local change of temperature $\delta_l T$ in the atmospheric column. We have:

$$\delta_l T = \delta_i T - \frac{\partial T}{\partial z} \cdot \delta z = \delta_i T + \frac{\partial T}{\partial z} \cdot \frac{1}{\gamma} \cdot \int_0^z \frac{\pi}{p} \cdot dz$$

The individual change of temperature $\delta_i T$ consists of:

(1) Change of temperature ($\delta_a T$) due to the replacement of the individual element of air at z with temperature T by the new element with temperature T_a brought in by advection ($\delta_a T = T_a - T$);

(2) Change of temperature ($\delta_a' T$) of the element due to adiabatic compression from p to $p + \pi$.

From equation (43) we see that when $\delta_a p = 0$,

$$\delta_a T = \frac{T}{g\rho} \cdot \frac{d\pi}{dz} = \frac{R}{g} \cdot \frac{T^2}{p} \cdot \frac{d\pi}{dz}$$

Also:

$$\delta_{a'} T = \frac{AR}{c_p} \cdot \frac{T}{p} \cdot \pi$$

Hence we have:

$$\delta_l T = \frac{R}{g} \cdot \frac{T^2}{p} \cdot \frac{d\pi}{dz} + \frac{AR}{c_p} \cdot \frac{T}{p} \cdot \pi + \frac{\partial T}{\partial z} \cdot \frac{1}{\gamma} \int_0^z \frac{\pi}{p} \cdot dz \qquad (55)$$

11. Advection Theory of Ertel and Sjan-zsi-Li

Ertel and Sjan-zsi-Li have criticised the general advection theory of Rossby because when applied to practical cases, it turns out that according to this theory, more than half the day to day variations of surface pressure have to be attributed to changes of mass above 12 to 14 kms. In particular they refer to an example discussed by Thomas, relating to the results of sounding balloon ascents over Lindenberg during the period 13th to 17th January 1930. Between these two dates there was an increase of surface pressure by 35 mms. of Hg over Lindenberg. When Rossby's general advection theory is applied to this case it appears that more than three-fourths of the observed increase of surface pressure has to be attributed to advection of mass above 15 kms. Since the atmospheric pressure at this height is only of the order of 90 mms. of Hg, such a result is highly improbable.

Ertel and Li have therefore concluded that there is a fundamental error in Rossby's general advection theory. They have preceded to work out new advection theory which gives the result:

$$\delta_l p = \pi(z) \left[1 - \frac{g\rho}{\gamma} \int_0^z \frac{dz}{p}\right], \qquad (56)$$

where $\delta_l p$ is the local change of pressure at the height z and $\pi(z)$ is the advective mass transport above this level. It will be seen that equation (56) is identical with equation (28) of Rossby's special advection theory, when addition of mass takes place *above* a height H, ($z < H$) so that $\pi(z)$ is a constant for $z < H$. In general, however, $\pi(z)$ is a function of the height z.

Let us now examine the assumptions implicit in the advection theory of Ertel and Li. It follows from equation (56) that when $\pi(z) = 0$, then $\delta_l p$ is also equal to zero. That is, *the pressure variation at any level* z *is independent of addition or removal of mass below that level.* It is clear that if we make this assumption then equation (56) follows at once from equation (28). However, this assumption is *not* generally correct. It is true only in the very special case in which the adiabatic compression of every individual element in the column at a height z ($z < z$) due to advective increase

of mass between z and z is exactly compensated by the adiabatic expansion of the element due to change in its internal pressure as a result of advection in the element. That is:

$$-\frac{1}{\gamma}[\pi(z)-\pi(z)]\frac{\Delta z}{p}=\frac{1}{\gamma}\delta_a p\,\frac{\Delta z}{p}$$

Hence, integrating:

$$-\frac{1}{\gamma}\int_0^z[\pi(z)-\pi(z)]\frac{dz}{p}=\frac{1}{\gamma}\int_0^z\delta_a p\cdot\frac{dz}{p}$$

Or:

$$-\frac{1}{\gamma}\int_0^z\pi(z)\frac{dz}{p}+\frac{1}{\gamma}\int_0^z\delta_a p\cdot\frac{dz}{p}=-\frac{1}{\gamma}\pi(z)\int_0^z\frac{dz}{p}$$

Comparing with (46) and (47), we see that the left-hand side of the above equation is equal to $\alpha+\beta=\delta z$. Hence:

$$\delta_l p=\pi(z)-\frac{\partial p}{\partial z}\cdot\delta z=\pi(z)\left[1-\frac{g\rho}{\gamma}\int_0^z\frac{dz}{p}\right]$$

We thus see that the advection theory of Ertel and Li is *not* a general theory as claimed by them. On the other hand, their theory is not applicable to cases of arbitrary advection.

Ertel and Li have applied their theory to the example discussed by Thomas and find that the results are in agreement with the calculations made by Thomas. They have remarked that his fact constitutes a strong support for their theory since they think that Thomas has tackled the problem in a different way, namely by making use of the observed equality of pressure at 15 kms. on the 13th and 17th January 1930. An examination of the calculations made by Thomas shows that this is not the case. Thomas has tacitly assumed in equations (8), (9) and (10) of his paper that the variation of pressure at a level is caused *entirely* by change of mass *above* that level. The assumption on which his computations are based is therefore the same as that implicit in the advection theory of Ertel and Sjan-zsi-Li. Hence it is not surprising that the results of Thomas agree with the formula of Ertel and Li, and this agreement cannot be regarded as independent support for the theory.

12. Some General Remarks

While the advection theory of Ertel and Li is not generally valid, the general advection theory of Rossby is perfectly correct under the assumptions

on which it is built up. If the theory leads to unreasonable results then, this must be attributed to the non-validity of the assumptions made. Rossby has explicitly stated the following assumptions:

(1) all movements are adiabatic, radiation, heat conduction, turbulence, condensation and evaporation phenomena being excluded;

(2) no lateral expansion or contraction of the column takes place;

(3) advection at one level is independent of simultaneous advection at other levels;

(4) a layer of thickness dz is through the advection process replaced by another layer of the same thickness.

Rossby has also stated that while the first of the above assumptions is generally justified, there can be large deviations from the conditions postulated by the remaining assumptions ; hence, the assumptions made restrict the applicability of the theory to a special class of advection phenomena.

As a consequence of his assumption (3) Rossby assumes that in (4) above, *the pressure at the upper boundary of the advection layer dz remains constant during the displacement.* This single assumption is practically the foundation stone of Rossby's theory and as we shall show below, is responsible for the unreasonable results to which the theory leads.

Referring to Fig. 4, let an addition of mass $\Delta M = \frac{\Delta \pi}{g}$ take place in an air column between the levels z and $z + \Delta z$. According to Rossby's theory, the column below z will be adiabatically compressed and the individual surface z will sink through the distance:

$$\delta a = -\frac{1}{\gamma} \cdot \Delta \pi \int_0^z \frac{dz}{p}$$

Rossby assumes that the entire column above z will ***bodily*** sink through the distance δa. As we have seen in Section 8, this will be the case only if the pressure at the upper boundary of the advection layer remains unaltered, that is, if $\delta_a p = 0$. In this case we have:

$$\Delta \pi = g \cdot \delta_a \rho \cdot \Delta z = g\rho \cdot \Delta z \cdot \frac{\delta_a T}{T} = g \cdot \frac{p}{RT^2} \cdot \delta_a T \cdot \Delta z$$

This means that the advective increase of mass between z and $z + \Delta z$ is caused *entirely* by the replacement of the original air by a different sample of air having the same pressure but a lower temperature. According to Rossby's theory, therefore, if $\delta_a T = 0$, then $\Delta \pi = 0$.

Referring to equation (6) in Section 2, we see that the general advection term responsible for change of mass in an element *dz* of an air column is given by:

$$\frac{\partial}{\partial x}(\rho u)+\frac{\partial}{\partial y}(\rho v)$$

$$=\left(u\frac{\partial \rho}{\partial u}+v\frac{\partial \rho}{\partial y}\right)+\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right)$$

$$=u\frac{\partial}{\partial x}\left(\frac{p}{RT}\right)+v\frac{\partial}{\partial y}\left(\frac{p}{RT}\right)+\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right)$$

$$=\frac{1}{RT}\left(u\frac{\partial p}{\partial x}+v\frac{\partial p}{\partial p}\right)-\frac{p}{RT^2}\left(u\frac{\partial T}{\partial x}+v\frac{\partial T}{\partial p}\right)+\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right)$$

Thus, the advection of mass in the element can be interpreted as resulting from three causes, *viz.*:

(i) Advection of air of the same temperature but different pressure;

(ii) Advection of air of the same pressure but different temperature;

(iii) Horizontal convergence or divergence of velocity.

Rossby's theory takes account of only (ii) above.

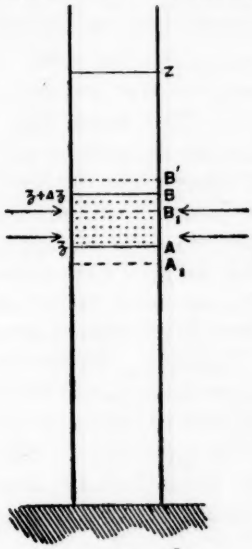


FIG. 6

To see how Rossby's theory can give rise to erroneous results, let us assume that (i) and (ii) above are zero, and (iii) alone is operative. In this case (*vide* Fig. 6), the increase of mass in the element Δz in time dt is given by:

$$\rho \left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right) dt \cdot \Delta z = \frac{\Delta \pi}{g}.$$

Increase of density inside the element $(\delta_a \rho) = \frac{1}{g}\frac{\Delta \pi}{\Delta z} = -\frac{1}{g}\frac{d\pi}{dz}$.

Increase of pressure inside the element $(\delta_a p) = \mathrm{RT} \cdot \delta_a \rho = -\frac{\mathrm{RT}}{g} \cdot \frac{d\pi}{dz}$.

As a consequence of the addition of mass, the column below z will be adiabatically compressed and the individual surface z will move downwards through the distance:

$$\delta\alpha = -\frac{1}{\gamma} \cdot \Delta\pi \int_0^z \frac{dz}{p}$$

At the same time, the stratum between z and $z + \Delta z$ will expand adiabatically (*vide* Section 8) through the distance:

$$\delta\beta = \frac{1}{\gamma} \cdot \delta_a p \cdot \frac{\Delta z}{p}.$$

The net downward displacement of the individual layer at z is given by:

$$\delta z = \delta\alpha + \delta\beta.$$

Since $\delta\alpha$ and $\delta\beta$ are opposite in sign and $\delta\alpha$ is negative, $\delta z > \delta\alpha$. Let us assume that δz is positive. This means that the entire column above z is bodily lifted up through the distance δz and so there will be a ***local increase*** of pressure at all levels above the layer of advection. A sounding through the column before and after the advection will therefore show local increase of pressure at ***all*** levels. If we apply Rossby's equation (54) to this case, it will be seen that we get a finite value of π greater than $\delta_l p$ at ***all*** levels in the column. With increasing height and decreasing values of $\delta_l p$, the value of π will tend towards a constant determined by the limiting value of the integral in Rossby's equation. We would thus be led to the obviously erroneous result that an appreciable part of the observed increase of pressure at the surface is due to addition of mass at levels at which the absolute value of pressure is small. Thus, by neglecting the effect of horizontal convergence and divergence of velocity, Rossby's theory over-emphasises the importance of the higher levels,—a feature which led Ertel and Li to seek a flaw in Rossby's theory.

The author was led to the present investigation as the result of a discussion with Diwan Bahadur Dr. K. R. Ramanathan in May 1945.

Summary

The paper contains a critical survey of the problem of pressure and temperature fluctuations in the atmosphere. If we exclude non-adiabatic processes, then changes of pressure and temperature are essentially due to horizontal and vertical movements in the atmosphere. The vertical distribution of pressure over the globe shows that horizontal movements (advection) can give rise to large changes of pressure especially in the middle latitudes. The problem of identifying the layer or layers in which addition or removal of mass has taken place due to advection, from the data furnished by aerological ascents over a station has been tackled by a number of investigators. Rossby considered the general problem of advection in several layers of an atmospheric air column, but his theory when applied to practical cases yields results which are often unreasonable. Ertel and Sjan-zsi-Li considered the same problem some years later and claimed to have discovered a fundamental error in Rossby's theory. In the present paper this problem is considered at some length. It is shown that Rossby's theory is quite correct under the assumption on which it is built up while the theory of Ertel and Li is not valid for cases of arbitrary advection. It is shown that the neglect of horizontal advection of pressure and horizontal convergence and divergence of wind velocity is responsible for the obviously unreasonable results furnished by Rossby's theory when applied to actual examples.

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(*Note.*—Since this investigation was completed the author has come across a paper by Geirmundur Arnason entitled "Distribution of Mass Variations in Atmospheric Air Columns," published in *Meteorologiske Annaler*, Band I, Nr. 10. The theory of Ertel and Li has also been criticised by Arnason.)

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DETERMINATION OF THE MAGNETO-OPTIC ANOMALY OF SOME GLASSES

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Received for publication on October 16, 1946

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

Darwin and Watson (1927) have shown that in many substances the magnitude of the Faraday effect is expressible by a formula of the Becquerel type, *viz.*,

$$V = \gamma \lambda \frac{dn}{d\lambda} e/2mc,^2$$

where V is Verdet's constant, e and m are the electronic charge and mass respectively, c is the velocity of light, λ is the wavelength of light and n the refractive index of the subtstance. γ is a factor, called the magneto-optic anomaly, which is constant throughout the visible and the ultraviolet regions of the spectrum provided the contribution to the dispersive power made by the infra-red absorption bands is eliminated from the formula. No reference to the data for glasses appears in the paper of Darwin and Watson. The present investigation was undertaken to fill this gap in the literature and to find whether the Becquerel formula is valid for glasses and if so to ascertain how the magneto-optic anomaly depends on the composition of the glass. Most of our knowledge of the magneto-optic behaviour of glasses is due to du Bois (1894) and to Ingersol (1917). The former measured Verdet's constant for the sodium line λ 5893 in nine glasses, while the latter studied the dependence of the constant on the wavelength in five glasses. The present paper records the values of Verdet's constant determined for λ 5893, λ 5461 and λ 4358 with 18 optical glasses made by the firm of Schott at Jena as well as of their dispersive powers for a test of the validity of the Becquerel formula. The results disclose the existence of interesting relationships between the composition and the magneto-optic anomaly.

2. Materials and Methods

The specimens studied formed a set of eighteen optical glasses presented to Prof. Sir C. V. Raman by Messrs. Schott & Co., Jena, and had the form

of rectangular blocks 3 × 3 × 2 cm. having all but two of the sides polished. The thickness of each glass did not deviate by more than 0·003 cm. from 2·000 cm. Table I gives the list of glasses studied, their melting numbers, approximate composition and density as supplied by the manufacturers.

TABLE I

List of Glasses Studied

Serial No.	Melting No.	Chemical composition		Density	n_{5893}	100γ
		More than 10%	Less than 10%			
1	25188	SiO_2, B_2O_3, Al_2O_3, K_2O	Na_2O, F	2·3	1·46693	67
2	18415	SiO_2, B_2O_3, K_2O	Al_2O_3	2·3	1·49340	67
3	16776	SiO_2, K_2O	Al_2O_3, Na_2O, CaO	2·4	1·50228	73
4	23975	SiO_2, B_2O_3, ZnO	Al_2O_3, Na_2O	2·5	1·50933	72
5	24906	SiO_2, B_2O_3	Na_2O, K_2O, BaO	2·5	1·51714	71
6	22601	SiO_2, B_2C_3, Sb_2O_3	Al_2O_3, Na_2O, K_2O	2·7	1·52998	68·5
7	23125	SiO_2, Na_2O, PbO	ZnO	2·7	1·52686	78·7
8	22638	SiO_2, PbO	Na_2O, K_2O	2·9	1·54495	77·4
9	24464	SiO_2, ZnO, BaO	B_2O_3, Na_2O, K_2O, PbO	3·1	1·57000	74
10	19510	SiO_2, PbO	Na_2O, K_2O	3·2	1·56991	77
11	23355	SiO_2, B_2O_3, BaO	Al_2O_3, Na_2O	3·3	1·58950	67·0
12	20672	SiO_2, PbO	B_2O_3, Na_2O, K_2O	3·4	1·59813	77·4
13	22986	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·5	1·60620	76·2
14	23441	SiO_2, PbO	Na_2O, K_2O,	3·9	1·64712	77·6
15	23497	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·9	1·64917	77·4
16	23850	SiO_2, PbO	Na_2O, K_2O	4·4	1·7130	77
17	23590	SiO_2, PbO	Na_2O, K_2O	5·1	1·7850	78
18	S1075	SiO_2, PbO	B_2O_3, K_2O, Sb_2O_3	6·7	1·8900	78

The refractive indices of the glasses were determined with the aid of a Pulfrich refractometer. The differences in refractive indices for different wavelengths could be determined with an accuracy of 2 or 3 units in the fifth place of decimals. Even so, the dispersion values were accurate only to one or two per cent. The refractive indices were determined for λ 5893, λ 5461 and λ 4358 and the constants in the dispersion formula

$$n^2 = A + B\lambda^2/(\lambda^2 - \lambda^2_0)$$

were evaluated. The values of $\lambda \frac{dn}{d\lambda}$ for different wavelengths were calculated. As the glasses 16, 17 and 18 had refractive indices much higher than the prisms supplied with the refractometer, their dispersions are not so accurate as those of the other glasses. Table II gives the refractive indices and the values of $\lambda \frac{dn}{d\lambda}$ of the glasses for different wavelengths.

An electromagnet of the Rutherford type with the distance between the polepieces 22 mm. was used in the work. When 7 amperes were passed

TABLE II

Dispersion Data for Glasses

No.	n_{5893}	n_{5461}	n_{4358}	$\lambda\frac{dn}{d\lambda}_{5893}$	$\lambda\frac{dn}{d\lambda}_{5461}$	$\lambda\frac{dn}{d\lambda}_{4358}$
1	1·46693	1·46868	1·47575	0·02316	0·02482	0·03897
2	1·49340	1·49522	1·50266	0·02217	0·02509	0·04130
3	1·50228	1·50430	1·51262	0·02457	0·02879	0·04649
4	1·50933	1·51138	1·51968	0·02501	0·02912	0·04578
5	1·51714	1·51910	1·52715	0·02393	0·02782	0·04356
6	1·52998	1·53249	1·54295	0·03045	0·03584	0·05892
7	1·52686	1·52939	1·53992	0·03087	0·03592	0·05614
8	1·54495	1·54782	1·55999	0·03478	0·04103	0·06814
9	1·57000	1·57243	1·58273	0·02938	0·03481	0·05891
10	1·56991	1·57320	1·58712	0·03979	0·04712	0·07945
11	1·58950	1·59183	1·60171	0·02823	0·03331	0·05637
12	1·59813	1·60190	1·61801	0·04551	0·05408	0·09317
13	1·60620	1·60962	1·62408	0·04124	0·04883	0·08279
14	1·64712	1·65182	1·67209	0·05666	0·06754	0·1174
15	1·64917	1·65335	1·67116	0·05052	0·05986	0·1023
16	1·7130	1·7191	1·7434	0·074	0·089	0·159
17	1·7850	1·7932	1·8281	0·097	0·116	0·210
18	1·8900	1·8999	1·9430	0·123	0·149	0·282

through the coils of the magnet, a field of 17200 gauss was developed. A pair of wide-angle nicols were used as polariser and analyser and the angles measured were to 0·05 of a degree and this gave an accuracy of about ½%. It was considered that a greater accuracy was not necessary as the dispersions were accurate to 1% only. Conductivity water whose Verdet's constant is accurately known (V_{5461} = 0·01547 at 25° C.) was used as the standard for the determination of the field. 1·24 cm. of water gave a rotation of 3·30° when 7 amperes were passed through the coils of the magnet. The field developed was, therefore, 17200 gauss.

A sodium lamp and a mercury point-o-lite lamp with suitable filters were used as the different sources of light for the measurement of the Verdet's constant of the glasses. If the glasses were kept exactly normal to the incident light, it was difficult to determine the true crossing position when the magnetic field was put on. This was due to the fact that light which comes to the analyser after two reflections at the surfaces of the glass was not rotated through the same angle as that which came without any reflection. To avoid this the glasses were turned through a small angle (about ½°) away from the normal position. Usually a mean of about 20 readings was taken to determine each crossing position. Table III gives the actual rotation ρ due to a field of 17200 gauss), the Verdet's constant V, and the anomaly γ for the three wavelengths λ 5893, λ 5461 and λ 4358 for the 18 glasses.

TABLE III

Magneto-optic Data for Glasses

Serial No.	λ 5893			λ 5461			λ 4358		
	ρ in degrees	V min./cm. gauss	γ %	ρ in degrees	V min./cm. gauss	γ %	ρ in degrees	V min./cm. gauss	γ %
1	5·15	0·0149	64·2	5·80	0·0169	67·4	8·95	0·0260	66·3
2	5·10	0·0148	66·4	5·85	0·0170	67·8	9·5	0·0276	66·4
3	6·35	0·0185	74·6	7·35	0·0214	73·7	11·40	0·0332	71·0
4	6·25	0·0182	72·1	7·40	0·0215	73·3	11·25	0·0327	71·0
5	5·90	0·0172	71·2	7·00	0·0204	72·6	10·50	0·0305	69·6
6	7·25	0·0211	68·7	8·50	0·0247	68·5	13·85	0·0403	67·8
7	8·20	0·0239	76·7	9·80	0·0285	78·8	15·45	0·0449	79·4
8	9·35	0·0272	77·6	11·00	0·0320	77·4	18·25	0·0531	77·3
9	7·80	0·0227	76·6	8·95	0·0260	74·2	14·75	0·0429	72·3
10	10·65	0·0310	77·3	12·70	0·0369	77·8	21·10	0·0614	76·7
11	6·75	0·0196	69·0	7·70	0·0224	66·7	12·95	0·0377	66·3
12	12·25	0·0356	77·7	14·50	0·0422	77·4	24·80	0·0721	76·9
13	10·85	0·0316	76·0	12·95	0·0377	76·6	21·75	0·0633	75·9
14	15·10	0·0439	76·9	18·20	0·0529	77·8	31·75	0·0953	78·0
15	13·35	0·0388	76·3	16·05	0·0467	77·4	27·45	0·0799	77·5
16	19·80	0·0576	77	23·85	0·0694	77	42·25	0·123	77·0
17	26·15	0·0761	78	31·30	0·0910	78	56·45	0·164	78·0
18	33·25	0·0969	78	40·55	0·1180	78	76·75	0·223	78·0

3. DATA FOR FUSED SILICA AND QUARTZ

Cotton (1931) has determined the Verdet's constant of vitreous silica for three wavelengths, λ 5780, λ 5461 and λ 4358. The constants were re-determined for the above wavelengths as well as for λ 5893 using a plate of 8·40 mm. thickness. The values obtained were within ½% of those obtained by Cotton. $\lambda\, dn/d\lambda$ for this substance was calculated from the dispersion formula

$$n^2 = 1{\cdot}36112 + \frac{0{\cdot}74655\,\lambda^2}{[\lambda^2-(0{\cdot}107044)^2]} - 0{\cdot}01350\,\lambda^2,$$

where λ is expressed in microns. The last term which is due to the infra-red absorption is omitted in the calculation. Table IV gives the optical and

TABLE IV

Magneto-optic Data for Fused Quartz

Wavelength in A. U.	Refractive Index	Verdet's constant		γ%
		Cotton	Author	
5893	1·4585	..	0·01421	78·1
5780	1·4590	0·01479	0·01491	78·1
5461	1·4601	0·01671	0·01664	78·1
4358	1·4667	0·02602	0·02640	75·8

magneto-optical constants of vitreous silica for the four wavelengths mentioned above.

A large number of workers (1903, 1912, 1917) have devoted themselves to the study of the Verdet constant of quartz for different wavelengths in the spectrum. Actual measurements extend from 20000 A° to 2000 A°. $\lambda\, dn/d\lambda$ is calculated from the dispersion formula

$$n^2_w = 3{\cdot}53445 + \frac{008067}{[\lambda^2 - 0{\cdot}00127493]} + \frac{0{\cdot}002682}{[\lambda^2 - 0{\cdot}000974]} + \frac{127{\cdot}2}{[\lambda^2 - 108]},$$

where n_w is the ordinary refractive index and λ is the wavelength expressed in microns. Here also the last term is omitted in the calculation. Table V gives the Verdet's constant, and for the value of γ different wavelengths.

TABLE V

Magneto-optic Data for Crystalline Quartz

Wavelength	Refractive Index	Verdet's Constant	γ %
20000	1·5199	0·001266	71
16000	1·5270	0·002106	75·4
12000	1·5323	0·003727	75·1
8000	1·5383	0·008802	79·0
5893	1·5443	0·01664	78·9
5460	1·5462	0·01952	78·5
5085	1·5482	0·02257	77·1
4799·9	1·5501	0·02574	78·6
4358	1·5538	0·03081	78·5
4046	1·5572	0·03555	74·4
3612	1·5635	0·04617	74·5
2573	1·5962	0·1079	75·4
2194·6	1·6250	0·1586	69·9

4. DISCUSSION OF RESULTS

It will be seen from Table V that the Becquerel formula is obeyed by quartz for the visible spectrum. There appears to be a small drop in the value of γ in the infra-red and the ultra-violet regions, but more accurate measurements are needed before the data could be accepted as indicating a real variation of γ with wavelength in quartz. Although the data for fused quartz (Table IV) are not so extensive as those for crystal quartz, it is seen that γ is sensibly constant in the visible region. It is worthy of remark that the values of γ for fused quartz and crystal quartz are practically identical, and this is particularly remarkable in view of the large difference in density and refractive indices of the two substances.

An examination of Table III shows that the value of γ is independent of wavelength in many of the glasses. Nevertheless, there are a few glasses in the list (Nos. 1, 3, 9 and 11) in which γ is apparently not constant. Since these variations in γ mostly occur in glasses of low dispersive power, they may be ascribed to inaccuracies in the measurement of the refractive indices. But a more probable reason is that the dispersion due to the infra-red term has not been eliminated (as has been done in quartz and fused silica) in calculating the value of $\lambda\, dn/d\lambda$ for the glasses. The variation in the value of γ in glass No. 9 is probably too large to be explained on these lines. In general, however, one could say that most of the glasses studied obey the Becquerel formula, the γ value of each glass being approximately constant for the visible spectrum. The mean value of γ of each glass has been incorporated in Table I.

A study of Table I reveals many interesting facts. All the glasses which do not contain B_2O_3 or Al_2O_3 have values of γ lying between 76% and 78%, thus differing very little from the values for fused and crystalline quartz. This is all the more remarkable when one considers the large variations in composition, density and dispersive power of the glasses. For instance, in spite of the dispersion of glass No. 18 being four times that of glass No. 7 the γ factor is not appreciably different. The variations in content of PbO and ZnO—which are principally responsible for the large dispersion and high density in some of the glasses—do not appear to involve any noticeable variations in the magneto-optic anomaly.

The presence of B_2O_3 seems to have a large influence on the γ value of a glass. All borate glasses have low γ values, γ being lower in glasses having a higher percentage of B_2O_3. Glass No. 1 and No. 2 which contain more than 20% of B_2O_3 have lower γ values than glass No. 9 which has less than 10% B_2O_3. The results with glass 3 seem to suggest that Al_2O_3 also depresses the γ value of a glass. The simultaneous presence of B_2O_3 and Al_2O_3 is obviously the cause of the very low value of γ in glasses No. 2, 6 and 11. It would seem that the presence of trivalent elements not only diminishes the dispersive power of a glass but also has the effect of diminishing the magneto-optic rotation in a still greater proportion, and that on the other hand, γ is practically the same for all silicate glasses which do not contain the trivalent elements.

In conclusion, the author wishes to thank Prof. Sir C. V. Raman for his kind guidance and encouragement during this investigation.

5. Summary

The paper records the values of Verdet's constant determined for λ 5893, λ 5461 and λ 4358 with 18 silicate glasses made by Schott & Co., Jena. The dispersive powers of the glasses have also been measured. It is found that most of the glasses obey a modified Becquerel formula, in which the multiplying factor γ is practically constant over the visible spectrum. The γ factor for fused quartz and crystalline quartz for different wavelengths have also been calculated. It is found that the value of γ for both the substances is about 78%. All the glasses which do not contain B_2O_3 or Al_2O_3 have γ values lying between 76% and 78% in spite of large variations in composition, density and dispersive power, the presence of the heavy elements like Pb, Ba and Zn in varying proportions having no influence on the γ value. On the other hand, trivalent elements like Boron and Aluminum when present in glasses diminish γ to values between 67% and 74% depending on the amount of B_2O_3 or Al_2O_3 present.

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UMBILICAL PROJECTION*

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Received February 8, 1944
(Communicated by Prof. B. S. Madhava Rao, F.A.SC.)

THE purpose of the paper is to illustrate the use of Umbilical Projection and establish a few theorems relating to certain sets of circles and families of coaxal circles in a plane by making use of a number of known results in space.

We start with a quadric Q in space and note the following correspondence:

Space S.	Plane II
(i) A *plane* section of Q. ..	A *Circle.*
(ii) Two planes determine a *line.*	A *family* of coaxal circles is determined by two circles.
(iii) Lines in a plane ..	Families *having a circle common* will be said to be "*intersecting*".
(iv) *Conjugate* planes for Q.	*Orthogonal* circles.
(v) Planes through a *point* ..	A *congruence* of circles that have *One circle common with a general family* will be said to be *linear.*†
(vi) Tangent planes of a *quadric.*	*A congruence of circles* that have *two circles common with a general family* will be said to be *quadric.*†
(vii) Tangent planes of a *cone.*	A *series of circles* that have *two circles common with a linear congruence* will be said to be *conic.*†
(viii) Tangent planes of a *cubic developable.*	A *series of circles* that have *three circles* common *with a linear congruence* is said to be *cubic.*†

* Read at the meeting of the Mathematical Society of the Panjab University, held on the 16th March 1942, in continuation of the paper published by the author in the *Proc. Ind. Acad. Sci.*, Bangalore, 1942, 15A, No. 1.

† Coolidge, *A Treatise on the Circle and the Sphere*, pp. 161, 157, 159.

Space S.	Plane II
(ix) *Polar lines* for Q. ..	*Conjugate families* of coaxal circles.
(x) *Conjugate lines* for Q. ..	Two families will be said to be '*polar*' when the *conjugate* of one intersects the other. *The relation is mutual.*
(xi) A *self-polar tetrahedron* for Q.	*Four mutually orthogonal circles* will be said to form a '*self-orthogonal tetrad,*' *for the family determined by two of them is conjugate to that of the other two.*
(xii) *A self-conjugate pentad* for Q.	*Five circles, related in the manner that the circle orthogonal to three of them belongs to the family determined by the other two, will be said to form a 'self-orthogonal pentad'.*
(xiii) *A self-conjugate hexad* for Q.	*Six circles, related that the circle orthogonal to three of them and the other three belong to a linear congruence will be said to form a 'self-orthogonal hexad'.*
(xiv) *Moebius Tetrads* ..	*Two tetrads* of circles ABCD and $A_1B_1C_1D_1$ will be said to be *Moebius* if a circle of one tetrad, say A_1 and three of the other tetrad, say B, C, D, belong to a linear congruence. *The relation between the two is mutual.*
(xv) *Reciprocal Tetrahedra* for Q.	*Two tetrads* of circles ABCD and A'B'C'D' will be said to be *reciprocal* if a circle of one, say A' is orthogonal to three of the other, say B, C, D and A, A';···will be said to be *corresponding circles* while BC, B'C';···*Corresponding families.*
(xvi) A *set of eight associated planes.*	The *eight circles* common to three independent quadric congruences will be said to form a *set of associated circles.*
(xvii) A *hexagon* ..	*Six circles* in general give rise to 15 *families that arrange into* 60 *'hexads'*

Space S.	Plane II
	of the nature that every given circle belongs to *two families of a hexad.* Two families of a hexad will be said to be *opposite* if the four circles determining them belong one to each of the other four families of the hexad.
(xviii) *Double-six of lines*	.. *Two sets of six families each* will be said to form a *double-six* if five of one set are intersected by a family of the other set.
(xix) *Opposite edges of a tetrahedron*	Given a *tetrad of circles,* they determine six families, two of them will be said to be *opposite* if they include all the four circles. There are *three pairs of opposite families.*

Now we are in a position to state the following theorems on circles in a plane without giving the details of the corresponding propositions, in space, that are hinted in brackets *wherever necessary* at the end of the theorem.

1. (i) *A linear congruence of circles is determined by three circles* in the manner that all the circles that are orthogonal to the circle orthogonal to the given three belong to it.

(ii) *A family and a circle also determine a linear congruence.*

(iii) Two families belonging to a linear congruence intersect.

(iv) Two linear congruences have a family common.

(v) Three linear congruences have a circle common.

2. If A_1BCD, AB_1CD, ABC_1D, $ABCD_1$, $A_1B_1C_1D$, $A_1BC_1D_1$, $A_1B_1CD_1$ be tetrads of circles belonging to seven linear congruences respectively, A, B_1, C_1, D_1 also belong to a linear congruence (*Moebius tetrads*).

3. *If the families determined by pairs of circles AA', BB', CC' have a circle common, the circles common to the pairs of families BC, B'C', CA, C'A', AB, A'B' are coaxal and conversely. The theorem holds even if the six circles belong to a linear congruence* (*Desargue's theorem*).

4. Let A', B', C' be the circles of the families conjugate to those determined by the pairs of circles QR, RP, PQ common with the linear

congruence determined by the circles A, B, C such that the families AA′, BB′, CC′ have a circle common, then, if P′, Q′, R′ be the circles of the families conjugate to BC, CA, AB, common with the linear congruence PQR, the families PP′, QQ′, RR′ have a circle common (B3*, Ex. 8, p. 42).

5. (i) *Two circles, one from each of two given families can be found to be coaxal with a given circle.*

(ii) If OHD_1, O_1KB be circles of two families of coaxals, the three pairs of circles L, M; N, C; A, P of pairs of families OK, O_1H; HB, KD_1; D_1O_1, BO coaxal with a given circle D *belong to a linear congruence.* Let B_1 *be a circle of this congruence,* then the three pairs of circles L_1, M_1; A_1, P_1; N_1, C_1 of the above families coaxal with B_1 belong to *another linear congruence that will contain D. The tetrads ABCD and* $A_1B_1C_1D_1$ *obtained here are Moebius* (B3, Ex. 10, p. 63).

(iii) *If the given families intersect, then the three pairs of above families also intersect and the circles common to the pairs are coaxal* (*Pappus' theorem*).

6. (i) Given three families of coaxal circles, there are ∞' families intersecting them forming a system. The aggregate of the circles of the two systems of families form a quadric congruence such that each circle belongs to two families one from each system.

(ii) The circles common to a quadric congruence and a linear congruence form a conic series.

(iii) A linear congruence containing a family of a quadric congruence contains another also.

(iv) *Two quadric congruences can have two conic series, a family and a cubic series, two intersecting families and a conic series or four families common such that the two conic series have two circles common; the cubic series and the family also have two circles common.*

7. (i) *There are two families of coaxal circles intersecting four general families of coaxals.*

(ii) Take five arbitrary families of coaxal circles. By omitting each in turn we obtain five sets of four families each; and these four families have got two families intersecting them; we again have two circles one from each of these two families coaxal with a given circle; the ten circles so obtained belong to a linear congruence (B3, Ex. 14, p. 66).

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* B3 refers to H. F. Baker, *Principles of Geometry*, Vol. 3, here as well as in what follows.

(iii) If the five families intersect another family, then each set of four families has one other family intersecting them, the five families so obtained also intersect a new family. We thus obtain two sets of six families each forming a *double-six* (B3, p. 159).

8. If the pairs of opposite families of a *hexad determined by six given circles* be intersecting, the six families will belong to a quadric congruence in which case we shall have *six circles,* one from each family, *belonging to a conic series common* to this congruence and a linear congruence. These six circles *will also give rise to* 60 *hexads of families.* With the property that *the circles common to the pairs of opposite families of a hexad are coaxal* (*B3, Dandelin's figure of six generators of a quadric forming a skew hexagon leading to Pascal's theorem for hexagon inscribed in a conic,* p. 45).

9. *Given a tetrad of circles, we shall have two circles from each pair of opposite families of the tetrad coaxal with a given circle giving rise to six circles, similarly we have six other circles corresponding to another given circle. The twelve circles so obtained belong to a quadric congruence.* (B3, Ex. 17, p. 54.)

10. *If circles be drawn coaxal with a family of a given tetrad of circles passing through the points of intersection of the circles of the opposite family, the twelve circles so obtained belong to a quadric congruence.* (B3, Ex. 16, p. 54.)

11. *If PP'; Q,Q' be pairs of orthogonal circles and f, f' be the respective conjugate families of those determined by P, P' and Q, Q', then f, f', P, P', Q, Q' belong to a quadric congruence* (B3, Ex. 13, p. 52).

12. (i) If ABCD, A'B'C'D' be *two reciprocal tetrads of circles, the families determined by the pairs of corresponding circles AA', BB', CC', DD' belong to a quadric congruence called* ϕ (*ABCD*) (B3, Ex. 7, p. 41).

(ii) Consider the twelve points of intersection of the six pairs of circles of the tetrad ABCD. Three of these lying on A, B, C define a circle. We may thus, in thirty-two ways, specify four circles each of which contains three of the points, no two of these circles intersect in one of the twelve points. If we consider the family determined by D' and the circle through the three points chosen on A, B, C and the three families determined by A', B', C' taken respectively with the corresponding circles, the four families so obtained belong to a quadric congruence (B3, Ex. 15, Pp. 53).

13. *Cubic series of circles* (B3, pp. 129, 135, 140).

(i) *Six circles in general determine the series.* If seven circles of the series be common with a quadric congruence, the whole series belongs to the congruence.

(ii) We can have *two series belonging to a quadric congruence having five given circles common.*

(iii) Three independent, quadric congruences can be constructed to contain the six circles. A, B, C, A′, B′, C′ and containing the pairs of families determined by B′ C, BC′; CA′, C′A; AB′, A′B respectively, then these quadric congruences have further a family common which has got two circles common with the series determined by the above six circles.

(iv) *Given five circles and a family of circles, we can construct a series which contains the given circles and has two circles common with the family; but we cannot in general construct a series to contain four given circles and having two circles common with each of two given families unless the circles and the families belong to a quadric congruence; further a series can be constructed containing three circles, and having two circles common with each of three given families; again four families can have two circles common with a series containing two circles given.*

(v) *A unique cubic series exists having two circles common with each of five given families in general and containing a given circle; infinite number of such series exist if the families are intersected by some other family.*

(vi) *There exist ten families that will have two circles each common with both of two given cubic series, hence it can be shown that there exist six cubic series having each two circles common with every one of six given families in general* (B3, pp. 141–42).

14. *Set of eight associated circles* (B3, p. 154).

(i) *The quadric congruences having seven circles common have an eighth common.*

(ii) *The circles of two self-orthogonal tetrads and those of Moebius tetrads form two sets, hence Moebius tetrads can consist of two self-orthogonal tetrads in a special case.*

(iii) *The cubic series determined by six circles of the set will have two circles common with the family determined by the remaining circles of the set.*

(iv) If the circles of the set be denoted by 1, 2, 3, 4, 5, 6, 7, 8, the family common to the congruences (linear) determined by 123 and 567 intersects the family determined by the circles common to the family 34

and the congruence 678 and the circle common to 45 and 812; hence it follows that four families common to the pairs of congruences 123, 567, 234, 678, 345, 781, 456, 812 belong to a quadric congruence.

(v) Let 2, 3, 4, 5, 7, 8 be any six circles and 1 a further circle; let P, P'; Q, Q'; R, R' be the pairs of circles from the pairs of families 23, 57, 78, 34, 45, 82, coaxal with 1. The families QR', RP', PQ' and Q'R, R'P, P'Q belong to a quadric congruence. Let P_1, Q_1', R_1, P_1', Q_1, R_1' be the other circles, common with this congruence, of the families 23, 34, 45, 57, 78, 82 respectively, then the families P_1, P_1' Q_1Q_1', R_1R_1', have a circle common say 6 completing the set.

15. (i) *If* $x_i = 0$ $(i = 1, 2, 3)$ *be equations*† *of three independent quadric congruences,* $\theta^2 x_1 + \theta x_2 + x_3 = 0$ *represent a system of quadric congruences out of which there are eight of a particular type** *that are determined by a circle and a conic series, the eight circles determining these eight congruences form a set of associated circles* (*Math. Student,* June 1942, **X,** Q. 1809).

(ii) *If three quadric congruences of circles have a family common they have four more circles common, if they have a conic series common, tney have two more circles common* (B3, Ex, 4, p. 154).

16. (i) *If two pairs of opposite families of a tetrad of circles be conjugate the remaining families are also conjugate and the tetrad is self-orthogonal.*

(ii) *If two pairs of opposite families of a tetrad of circles be polar, the remaining families are also polar, similarly behave the reciprocal tetrad.*

(iii) *The families determined by the corresponding pairs of circles here have a new circle common forming with either of the tetrads a self-orthogonal pentad. The pairs of corresponding families are intersecting, giving six more circles that are orthogonal to the new circle obtained above. We have thus got* 15 *circles in all such that each one is orthogonal to six of them that are coaxal by threes forming four families. In fact, there are* 15 *circles,* 20 *families constituting* 10 *pairs of conjugate as well as polar families, and* 15 *linear congruences with the property that each circle belongs to four families and six congruences, each family contains three circles and belongs to three congruences, each congruence contains six circles and four families. The* 15 *centres of the circles are collinear by threes in* 20 *lines, four through each centre, forming* 15 *quadrilaterals whose vertices are the centres, each*

* Coolidge, *loc. cit.*, pp. 161 and 165, Th. 54.

vertex is common to six quadrilaterals which have a line common by threes. (B3, Ex. 5, p. 35).

17. As a special case we can construct *a self-orthogonal pentad consisting of three point-circles and two proper circles*: Let AB'CA'BC' be a hexagon such that every pair of adjacent sides are circular lines; if D, E, F be the meet of the opposite sides. the circles DEF, ABC and the point-circles A', B', C' or the circles DEF, A'B'C' and the point circles A, B, C form the required pentad. (B3, Ex. 9, p. 44.)

18. If ϕ (ABCE) be a quadric congruence constructed in the manner of § 12 where E is a circle of the congruence ϕ (ABCD), the two congruences have a family common, with D' as a member and ϕ (ABCE) contains the circle D. If F be the circle of ϕ (ABCE) common to the family having E as a member, intersecting the families AA', BB', CC', other than E, the *six circles ABCDEF form a self-orthogonal hexad. In particular, if the circles D', E, F are coaxal, the circles A B C E F form a self-orthogonal pentad* (B3, Ex. 10, p. 47).

19. *A self-orthogonal tetrad or pentad taken with any other circle form a self-orthogonal pentad or hexad of circles respectively.*

20. *If the circles of either a self-orthogonal tetrad, pentad or hexad belong to a quadric congruence or a cubic series, an infinite number of such sets of circles can be found to belong to the congruence or the series.* (B3, Ex. 12, p. 50; Ex. 27, p. 145).

21. *Let a, b, c be the linear congruences of circles orthogonal to the circles A, B, C respectively, and p, q, r be the families of coaxals common to the pairs of congruences b, c; c, a; a, b respectively; then the congruences Ap, Bq, Cr have a family common.*

22. *If a variable family of coaxals moves about so that three fixed circles of it belong to three fixed linear congruences respectively, any fourth fixed circle of the family will then generate a quadric congruence.* (*Salmon*, Vol. I, p. 118, Ex. 14).

23. *If the variable families of a hexad contain each a fixed circle and five circles of the hexad belong each to a linear congruence, the sixth circle of the hexad then generates a cubic series* (*Salmon*, Vol. I, Ex. 5, p. 145).

A CONGRUENCE PROPERTY OF $\tau(n)$

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Received August 27, 1946

(Communicated by Prof. B. S. Madhava Rao)

Ramanathan and, more recently, Bambah and Chowla have proved by different methods involving the use of certain relations between Ramanujan's functions P, Q and R, that

$$\tau(n) \equiv n\sigma_3(n) \pmod 7 \tag{1}$$

where $\tau(n)$ is defined by the relation

$$\sum_1^\infty \tau(n)\, x^n = x\{(1-x)(1-x^2)(1-x^3)\ldots.\}^{24}, \quad |x| < 1; \tag{2}$$

and

$$\sigma_3(n) = \sum_{d|n} d^3. \tag{3}$$

I give below a proof which is independent of such relations. All congruences are modulo 7.

We have

$$\sum_1^\infty \tau(n)\, x^n = x\{\prod_1^\infty (1-x^r)\}^{21}\{\prod_1^\infty (1-x^r)\}^3$$

$$\equiv x\{\prod_1^\infty (1-x^{7r})\}^3\{\prod_1^\infty (1-x^r)\}^3$$

$$\equiv x\{\sum_{u=0}^\infty (-1)^u (2u+1)\, x^{7u(u+1)/2}\}\{\sum_{v=0}^\infty (-1)^v (2v+1)\, x^{v(v+1)/2}\}.$$

Hence

$$\tau(n) \equiv \sum (-1)^{u+v}(2u+1)(2v+1) \tag{4}$$

where u, v run through the non-negative solutions of the equation

$$n = 1 + \frac{7u(u+1)}{2} + \frac{v(v+1)}{2}$$

which can be put in the form

$$8n = 7(2u+1)^2 + (2v+1)^2. \tag{5}$$

If $\left(\frac{n}{7}\right) = -1$, (5) has no solution. Therefore

$$\tau(n) \equiv 0 \text{ when } n^3 \equiv -1. \tag{6}$$

Also if $n \equiv 0$, then from (5)

$$2v + 1 \equiv 0.$$

Hence

$$\tau(7m) \equiv 0. \tag{7}$$

Now consider the case when n is equal to an odd prime p other than 7, such that

$$\left(\frac{p}{7}\right) = 1.$$

Then the equation

$$p = x^2 + 7y^2 \tag{8}$$

has a unique solution in positive integers x, y of opposite parity. If (x_1, y_1) be this solution, then

$$8p = (x_1 + 7y_1)^2 + 7(x_1 \sim y_1)^2 = (x_1 \sim 7y_1)^2 + 7(x_1 + y_1)^2 \tag{9}$$

provides the two solutions of (5), giving

$$\tau(p) \equiv 2x_1^2 \equiv 2p \equiv p(p^3 + 1). \tag{10}$$

In view of the relations (6), (7) and (10), we have

$$\tau(p) \equiv p\sigma_3(p) \tag{11}$$

for all primes $p > 2$. It holds also when $p = 2$ because

$$\tau(2) = -24 \equiv 18 = 2\sigma_3(2).$$

Using Mordell's identity

$$\tau(p^\lambda) = \tau(p)\tau(p^{\lambda-1}) - p^{11}\tau(p^{\lambda-2}), \quad \lambda \geqslant 2,$$

it is now easily shown that

$$\tau(p^\lambda) \equiv p^\lambda \sigma_3(p^\lambda).$$

Since $\tau(n)$ and $\sigma_3(n)$ are both multiplicative functions

$$\tau(n) \equiv n\sigma_3(n).$$

SOME CONGRUENCE PROPERTIES OF THE ϕ-FUNCTION

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Received August 6, 1946

(Communicated by Prof. B. S. Madhava Rao)

Let $\phi(n)$ denote the number of numbers not greater than and prime to n. Then the following lemma can easily be proved:

Lemma 1.—If a and b are prime to n and m is the least positive integer for which

$$a^m \equiv b^m \bmod n,$$

then every integer N such that

$$a^N \equiv b^N \bmod n$$

is a multiple of m; in particular $\phi(n)$ is a multiple of m.

We now proceed to prove the following:

Theorem 1.—If a is greater than and prime to b, then

$$\phi(a^n - b^n) \equiv 0 \bmod n.$$

For, obviously

$$a^n \equiv b^n \bmod (a^n - b^n);$$

and if $r < n$, then $a^r - b^r < a^n - b^n$, so that

$$a^r \not\equiv b^r \bmod (a^n - b^n).$$

It follows from lemma 1 that n is a divisor of $\phi(a^n - b^n)$.

Theorem 2.—If a is prime* to b and $n \geqslant 2$, then

$$\phi\{a^{m(n-1)} + a^{m(n-2)} b^m + a^{m(n-3)} b^{2m} + \ldots + b^{m(n-1)}\} \equiv 0 \bmod mn.$$

Proof.—It is clear that

$$a^{mn} - b^{mn} \equiv 0 \bmod \{a^{m(n-1)} + a^{m(n-2)} b^m + \ldots + b^{m(n-1)}\} \qquad (1)$$

If N is the least positive integer such that

$$a^N - b^N \equiv 0 \bmod \{a^{m(n-1)} + a^{m(n-2)} b^m + \ldots + b^{m(n-1)}\} \qquad (2)$$

then, by lemma 1, N is a divisor of mn. Also, for $N < m(n-1)$,

$$|a^N - b^N| < a^{m(n-1)} + a^{m(n-2)} b^m + \ldots + b^{m(n-1)}$$

* Here, as well as in what follows we shall exclude the case $a = b = 1$.

Therefore

$$mn \geqslant \mathrm{N} \geqslant m(n-1). \tag{3r}$$

Let g be the g.c.d. of m and N and let

$$m = gm_1, \ \mathrm{N} = g\mathrm{N}_1.$$

Writing $a^g = \alpha$ and $b^g = \beta$ we see from (2) that N_1 is the least positive intege) such that

$$\alpha^{\mathrm{N}_1} \equiv \beta^{\mathrm{N}_1} \bmod \{\alpha^{m_1(n-1)} + \alpha^{m_1(n-2)}\beta^{m_1} + \ldots + \beta^{m_1(n-1)}\}.$$

It follows that N_1 is a divisor of $m_1 n$, and since N_1 is prime to m_1, that N_1 is a divisor of n. But from (3) we see that

$$\mathrm{N}_1 \geqslant m_1(n-1) \geqslant (n-1).$$

Hence $\mathrm{N}_1 = n$, $m_1 = 1$, and so $m = g$, $\mathrm{N} = mn$.

Therefore, by lemma 1, mn is a divisor of

$$\phi\{a^{m(n-1)} + a^{m(n-2)}b^m + \ldots + b^{m(n-1)}\}.$$

2. Let $n = p^a n_1$, where p is prime and n_1 is prime to p. Then if we write

$$f(m, n) = a^{m(n-1)} + a^{m(n-2)}b^m + \ldots + b^{m(n-1)}$$

we have

Lemma 2.—$a^n - b^n = (a^{n_1} - b^{n_1}) \prod_{i=1}^{a} f(n/p^i, p)$.

Let us further suppose that a is prime to b. Then we have

Lemma 3.—The g.c.d. of any two of the numbers

$$a^{n_1} - b^{n_1}, \ f(n/p^i, p) \ (i = 1, 2, \ldots, a)$$

is either p or 1.

For, if d is a common divisor of

$$f(n/p^j, p) \text{ and } f(n/p^i, p) \ (i < j),$$

then

$$0 \equiv f(n/p^j, p)\,(a^{n/p^j} - b^{n/p^j})$$

$$\equiv a^{n/p^{j-1}} - b^{n/p^{j-1}} \bmod d;$$

and so

$$0 \equiv f(n/p^i, p) \equiv pa^{n(p-1)/p^i} \bmod d$$

so that, since d is prime to a,

$$d = p \text{ or } 1.$$

Similarly we can show that the g.c.d. of

$$a^{n/p^\alpha} - b^{n/p^\alpha} \text{ and } f(n/p^i, p)$$

is either p or 1.

Lemma 4.—$f(n/p^i, p) \equiv f(n/p^\alpha, p) \bmod p$ $(i = 1, 2, \ldots, \alpha)$.

This follows immediately from

$$a^{n/p^i} = a^{p^{\alpha-i}\, n/p^\alpha} \equiv a^{n/p^\alpha} \bmod p.$$

Lemma 5.—If $f(m, p) \equiv 0 \bmod p$, then

$$a^m \equiv b^m \bmod p.$$

For,

$$0 \equiv f(m, p)(a^m - b^m) = a^{mp} - b^{mp} \bmod p,$$

and

$$a^{mp} \equiv a^m \bmod p$$

$$b^{mp} \equiv b^m \bmod p$$

so that

$$0 \equiv a^{mp} - b^{mp} \equiv a^m - b^m \bmod p.$$

Conversely, we have

Lemma 6.—If $a^m \equiv b^m \bmod p$, then

$$f(m, p) \equiv 0 \bmod p.$$

From lemmas 2 to 6 we get

Lemma 7.—If any one of

$$a^{m_1} - b^{m_1},\ f(n/p^i, p) \qquad (i = 1, 2, \ldots, \alpha)$$

is prime to p, then they are all prime to each other, and

$$\phi(a^n - b^n) = \phi(a^{m_1} - b^{m_1}) \prod_{i=1}^{\alpha} \phi\{f(n/p^i, p)\}$$

Similarly we get

Lemma 8.—If any one of $a^{m_1} - b^{m_1}, f(n/p^i, p)$ $(i = 1, 2, \ldots, \alpha)$ is divisible by p, then so are all of them and

$$(a^{m_1} - b^{m_1})/p,\ f(n/p^i, p)/p \quad (i = 1, 2, \ldots, \alpha)$$

are prime to each other; further, $a^n - b^n$ is divisible by $p^{\alpha+1}$ and

$$\phi\{(a^n - b^n)/p^{\alpha+1}\} = \phi\{(a^{m_1} - b^{m_1})/p\} \prod_{i=1}^{\alpha} \phi\{f(n/p^i, p)/p\}.$$

Lemma 9.—None of

$$f(n/p^i, p) \quad (i = 1, 2, \ldots, \alpha - 1)$$

is divisible by a higher power of p than the first.

If one of a, b is a multiple of p, then the other is not, and so $f(n/p^i, p)$ is clearly prime to p. Therefore we may assume that a and b are both prime to p. Then

$$\frac{n}{a^{p^i}}\left(1-\frac{1}{p}\right) \equiv 1 \bmod p^2, \ \alpha > i+1$$

i.e.,

$$a^{n/p^i} \equiv a^{n/p^{i+1}} \bmod p^2, \ \alpha > i+1,$$

and so

$$f(n/p^i, p) = f(n/p^{i+1}, p) \bmod p^2, \ i < \alpha - 1.$$

It follows that if any one of $f(n/p^i, p)$ $(i = 1, 2, \ldots, \alpha - 1)$ is divisible by p^2, then so are all the others; but this cannot be the case because of lemma 3.

We are now in a position to prove

THEOREM 3.—If $n = p^\alpha n_1$ where p is the smallest prime factor of n, and n_1 is prime to p, and a is greater than and prime to b, then

$$\phi(a^n - b^n)$$

is divisible by

$$\phi(a^{n_1} - b^{n_1})\, n^\alpha / p^{\alpha(\alpha-1)/2} \text{ if } a^n - b^n \text{ is prime to } p,$$

and by

$$\phi(a^{n_1} - b^{n_1})\,(pn)^\alpha / p^{\alpha(\alpha-1)/2} \text{ if } p \text{ is a divisor of } a^n - b^n.$$

Proof.—If any one of $a^{n_1} - b^{n_1}$, $f(n/p^i, p)$ $(i = 1, 2, \ldots, \alpha)$ is prime then by lemma 7 we have

$$\phi(a^n - b^n) = \phi(a^{n_1} - b^{n_1}) \prod_{i=1}^{\alpha} \phi\{f(n/p^i, p)\}.$$

But, by theorem 2,

$$\phi\{f(n/p^i, p) \equiv 0 \bmod n/p^{i-1},$$

and so

$$\phi(a^n - b^n) \equiv 0 \bmod \phi(a^{n_1} - b^{n_1}) \prod_{i=1}^{\alpha} n/p^{i-1}.$$

If, on the other hand, $a^{n_1} - b^{n_1}$, $f(n/p^i, p)$ are all divisible by p, then by lemma 8

$$\phi\{(a^{n_1} - b^{n_1})/p^{\alpha+1}\} = \phi\{(a^{n_1} - b^{n_1})/p\} \prod_{i=1}^{\alpha} \phi\{f(n/p^i, p)/p\}.$$

But $f(n/p^i, p)/p$ being prime to p for $i < \alpha$, (by lemma 9)

$$\phi\{f(n/p^i, p)\} = \phi\{f(n/p^i, p)/p\}\,\phi(p),$$

and so, by theorem 2

$$\phi\{f(n/p^i, p)/p\} \equiv 0 \bmod n/p^{i-1}, \ i < \alpha,$$

since every prime factor of n/p^{i-1} is greater than $\phi(p) = p - 1$. Further, if the greatest power of p dividing $a^n - b^n$ be $p^{\alpha+1+r}$ $(r \geqslant 0)$, then either

$a^{n_1} - b^{n_1}$ or $f(n_1, p)$ is divisible by p^{r+1} and

$$\phi(a^n - b^n) = \phi(p^{\alpha+1+r})\,\phi[(a^n - b^n)/p^{\alpha+1+r}]$$

$$= \begin{cases} p^{\alpha+1}\,\phi[(a^n - b^n)/p^{\alpha+1}] & \text{if } r \geqslant 1 \\ p^{\alpha}(p-1)\,\phi[(a^n - b^n)/p^{\alpha+1}] & \text{if } r = 0; \end{cases}$$

and

$$\phi(a^{n_1} - b^{n_1}) = \phi(p^{r+1})\,\phi[(a^{n_1} - b^{n_1})/p^{r+1}]$$

$$= \begin{cases} p\,\phi[(a^{n_1} - b^{n_1})/p] & \text{if } r \geqslant 1, \\ (p-1)\,\phi[(a^{n_1} - b^{n_1})/p & \text{if } r = 0. \end{cases}$$

It follows that

$$\phi(a^n - b^n) = p^{\alpha}\,\phi(a^{n_1} - b^{n_1}) \cdot \frac{\phi[(a^n - b^n)/p^{\alpha+1}]}{\phi[(a^{n_1} - b^{n_1})/p]}$$

$$= p^{\alpha}\,\phi(a^{n_1} - b^{n_1}) \prod_{i=1}^{\alpha} \phi\{f(n/p^i, p)/p\}$$

$$\equiv 0 \bmod p^{\alpha}\,\phi(a^{n_1} - b^{n_1}) \prod_{i=1}^{\alpha} n/p^{i-1},$$

since $\phi\{f(n_1, p)/p\}$ is certainly divisible by $n_1 p$ by Theorem 2 whether $f(n_1, p)$ is divisible by a higher power of p than the first ore not, from the fact that n_1 is prime to $\phi(p)$. This completes the proof of the theorem.

From theorem 3 we get the following refinement of theorem 1.

THEOREM 4.—If $n = p_1^{\alpha_1} p_2^{\alpha_2} \ldots p_r^{\alpha_r}$, where $p_1 > p_2 > \ldots > p_r$ are the distinct prime factors of n, and a is greater than and prime to b, then

$$\phi(a^n - b^n) \equiv 0 \bmod \prod_{i=1}^{r} p_i^{\alpha_i(\alpha_1 + \alpha_2 + \cdots + \alpha_{i-1}) + \frac{\alpha_i(\alpha_i+1)}{2}}$$

Proof.—From theorem 3 we have

$$\phi(a^n - b^n) \equiv 0 \bmod \phi(a^{n/p_1^{\alpha_1}} - b^{n/p_1^{\alpha_1}}) \times n^{\alpha_1}/p_1^{\alpha_1(\alpha_1-1)/2}.$$

Since p_2 is the least prime factor of $n/p_1^{\alpha_1}$ we have similarly

$$\phi(a^{n/p_1^{\alpha_1}} - b^{n/p_1^{\alpha_1}}) \equiv 0 \bmod \phi(a^{n/p_1^{\alpha_1} p_2^{\alpha_2}} - b^{n/p_1^{\alpha_1} p_2^{\alpha_2}}) \times \left(\frac{n}{p_1^{\alpha_1}}\right)^{\alpha_2} \Big/ p_2^{\alpha_2(\alpha_2-1)/2}$$

and so on. Thus

$$\phi(a^n - b^n) \equiv 0 \bmod \prod_{i=1}^{r} \left(\frac{n}{p_1^{\alpha_1} \ldots p_{i-1}^{\alpha_{i-1}}}\right)^{\alpha_i} \Big/ p_i^{\alpha_i(\alpha_i-1)}$$

which is easily seen to be theorem 4.

DETERMINATION OF MAGNESIUM AND RESIDUAL MANGANESE IN ROCKS AND MINERALS WITH 8-HYDROXY-QUINOLINE

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Received September 28, 1946

Neelakantam[1] published recently procedures for the gravimetric determination of manganese, and of magnesia and residual manganese as they occur together in the analysis of rocks and minerals by means of 8-hydroxy-quinoline. In the latter case the manganese content was determined colorimetrically. Satisfactory results were obtained for both magnesia and manganese. This investigation was, however, carried out on pure solutions of the salts and the conditions obtaining in rock analysis were reproduced by adding oxalic acid, ammonium and sodium chlorides.

The present paper deals with the actual analyses of some rock and mineral samples, *viz.*, charnockite, leptynite and garnet by the above procedures and direct comparison of the results with those obtained by the usual pyrophosphate method.

Experimental

The finely ground sample (1·0 gm.) was weighed out accurately and opened up by fusion with sodium carbonate according to the procedure described by Harwood.[2] After eliminating the silica, the R_2O_3 hydroxides and lime and strontia, the filtrate was evaporated to dryness on the water-bath. The ammonium salts and oxalic acid were oxidised by means of concentrated nitric acid in the usual manner. The residue containing magnesia and the residual manganese was taken up in 5 c.c. of 2N hydrochloric acid and the solution made up to volume in a measuring flask (100 c.c.) with water. One aliquot (25 c.c.) was precipitated with ammonium phosphate according to standard procedure for Gibb's method[3] and the determination completed by ignition to the pyrophosphate and weighing. The manganese content of this residue was determined colorimetrically by the well known periodate method. An equal volume of the solution was precipitated with 8-hydroxy-quinoline according to the following procedure previously worked out by Neelakantam (*loc. cit.*).

To the solution containing magnesium and manganese, an excess of a 0·5% solution of oxine acetate (2N acetic acid) was added and heated to

60–70° C. Dilute ammonia was added dropwise with stirring until alkaline to litmus. Finally 3 c.c. of strong ammonia was added and the precipitate digested on the water-bath for one hour and cooled to laboratory temperature. The precipitate was filtered through a sintered glass crucible (No. 3), washed with hot dilute ammonia (1 : 40), dried to constant weight at 150° C. and weighed as anhydrous magnesium and manganese oxy-quinolinates. For the colorimetric estimation of manganese in this residue, the oxine complex was dissolved out in hot, dilute nitric acid, the solution evaporated to dryness in a platinum dish and the residue gently ignited to destroy the organic matter, moistening with concentrated nitric acid if necessary. The final residue was dissolved in a few drops of sulphurous acid, the manganese oxidised by periodate and nitric acid and estimated colorimetrically.

From the values obtained for manganese in both determinations, the magnesia contents were calculated by difference. The results are tabulated below:—

No.	Sample	MnO%		MgO%	
		Pyrophosphate Method	Oxine Method	Pyrophosphate Method	Oxine Method
1	Leptynite ..	0·05	0·09	1·82	1·80
2	Charnockite ..	0·07	0·09	9·01	9·02
3	Garnet ..	0·18	0·29	4·48	4·50

Discussion

It is to be noted that while the results obtained for magnesia by the two methods are in good agreement, the results for manganese by the oxine method of precipitation are definitely higher than by the pyrophosphate method. The explanation is to be found in the well known fact that the precipitation of manganese as the crystalline ammonium phosphate is generally incomplete, as much as 0·2 mg. or more escaping precipitation so that in accurate analyses it is customary to make final corrections based on colorimetric tests on the filtrate.[4] The oxine method obviously secures complete precipitation of residual manganese along with magnesia and gives more accurate results. The improvement is of considerable value in rock analysis, for the manganese content of the R_2O_3 is obtained by difference from the values for total and residual manganese and any error in its value reflects on the figure for alumina. Improved accuracy in the determination of

magnesia is also rendered possible by the oxine method as it is simple and the magnesium content of the anhydrous oxine complex is only 7·78%.

Summary

The magnesia and residual manganese have been precipitated together with oxine, the content of the latter determined colorimetrically and that of the former calculated by difference in the analyses of samples of charnockite, leptynite and garnet. The results obtained are compared with those obtained in parallel determinations carried out by the pyrophosphate method and improved accuracy in the estimation of residual manganese as well as magnesia claimed.

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CONDITIONS OF PLANE ORBITS IN CLASSICAL AND RELATIVISTIC FIELDS

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Received March 21, 1946

1. The classical equations for the motion of a test-particle in a field of force (X, Y, Z) are

$$\ddot{x} = X,\ \ddot{y} = Y,\ \ddot{z} = Z. \tag{1}$$

What are the restrictions on X, Y, Z as functions of (x, y, z, t) if the orbit of the test-particle is required to be *invariably* plane? This is a simple interesting question and as it does not appear to have been investigated before we consider it here.

If s denotes the distance of the current point, that is, the position of the test-particle on the orbit at time t from some fixed point on it we have

$$\begin{vmatrix} \frac{dx}{ds} & \frac{dy}{ds} & \frac{dz}{ds} \\ \frac{d^2x}{ds^2} & \frac{d^2y}{ds^2} & \frac{d^2z}{ds^2} \\ \frac{d^3x}{ds^3} & \frac{d^3y}{ds^3} & \frac{d^3z}{ds^3} \end{vmatrix} = \kappa^2\tau, \tag{3}$$

where κ and τ are the local curvature and torsion respectively. It readily follows that if the orbit is to be plane we must have everywhere on it

$$\begin{vmatrix} \dot{x} & \dot{y} & \dot{z} \\ \ddot{x} & \ddot{y} & \ddot{z} \\ \dddot{x} & \dddot{y} & \dddot{z} \end{vmatrix} = 0. \tag{3}$$

(1) and (3) lead to

$$\Sigma\dot{x}\left\{Y\left(\frac{\partial Z}{\partial x}\dot{x}+\frac{\partial Z}{\partial y}\dot{y}+\frac{\partial Z}{\partial y}\dot{z}+\frac{\partial Z}{\partial t}\right)-Z\left(\frac{\partial Y}{\partial x}\dot{x}+\frac{\partial Y}{\partial y}\dot{y}+\frac{\partial Y}{\partial z}\dot{z}+\frac{\partial Y}{\partial t}\right)\right\}=0. \tag{4}$$

The last equation can be valid at any point of the field for arbitrary values of the velocities only if

$$Y\frac{\partial Z}{\partial t}-Z\frac{\partial Y}{\partial t}=0,\quad Z\frac{\partial X}{\partial t}-X\frac{\partial Z}{\partial t}=0,\quad X\frac{\partial Y}{\partial t}-Y\frac{\partial X}{\partial t}=0, \tag{5}$$

$$Y\frac{\partial Z}{\partial x}-Z\frac{\partial Y}{\partial x}=0,\quad Z\frac{\partial X}{\partial y}-X\frac{\partial Z}{\partial y}=0,\quad X\frac{\partial Y}{\partial z}-Y\frac{\partial X}{\partial z}=0, \tag{6}$$

$$Y\frac{\partial Z}{\partial y}-Z\frac{\partial Y}{\partial y}-X\frac{\partial Z}{\partial x}+Z\frac{\partial X}{\partial x}=0,$$

$$Z\frac{\partial X}{\partial z}-X\frac{\partial Z}{\partial z}-Y\frac{\partial X}{\partial y}+X\frac{\partial Y}{\partial y}=0, \tag{7}$$

$$X\frac{\partial Y}{\partial x}-Y\frac{\partial X}{\partial x}-Z\frac{\partial Y}{\partial z}+Y\frac{\partial Z}{\partial z}=0,$$

From (5) and (6) it follows that:

$$\begin{aligned} X/Y &= \theta(x, y),\\ Y/Z &= \phi(y, z),\\ Z/X &= \psi(z, x), \end{aligned} \tag{8}$$

where θ, ϕ, ψ are arbitrary functions. One may safely conclude that X, Y, Z are of the form:

$$X = Pf(x),\ Y = Pg(y),\ Z = Ph(z), \tag{9}$$

where f, g, h are arbitrary functions of the variables concerned and P is an arbitrary function of x, y, z, t. Substituting for X, Y, Z from (9) in (7) we have

$$\frac{\partial f}{\partial x}=\frac{\partial g}{\partial y}=\frac{\partial h}{\partial z} \tag{10}$$

Hence

$$f = \lambda x + \epsilon_1,\ g = \lambda y + \epsilon_2,\ h = \lambda z + \epsilon_3, \tag{11}$$

where λ, ϵ_1, ϵ_2, ϵ_3 are arbitrary constants. Thus we find that the orbits are always plane in the field of force:

$$X = (\lambda x + \epsilon_1)P,\ Y = (\lambda y + \epsilon_2)P,\ Z = (\lambda z + \epsilon_3)P. \tag{12}$$

It is obvious that the forces are not derivable from a potential function unless P is of the form,

$$P = P(\chi, t), \tag{13}$$

where $$\chi = \lambda(x^2 + y^2 + z^2) + 2\epsilon_1 x + 2\epsilon_2 y + 2\epsilon_3 z + \eta, \tag{14}$$

η being an arbitrary constant.

It can be easily shown that if the forces (12) are supplemented by a resisting force the orbit still remains plane.

It is interesting to notice also that the condition for plane orbits leads to what Bergmann[1] calls the classical force law.

2. The above discussion of a classical field of force suggests an interesting mathematical problem, which appears rather artificial, but which is based all the same on the established practice in general relativity.[2] For a relativistic line-element of the form,

$$ds^2 = -e^{\lambda}\,dr^2 - r^2(d\theta^2 + \sin^2\theta d\phi^2) + e^{\nu}\,dt^2, \tag{15}$$

$$\lambda = \lambda(r, t), \quad \nu = \nu(r, t), \tag{16}$$

the geodesies provide three differential equations in r, θ, ϕ, t and the first and second order derivatives of r, θ, ϕ with respect to t. If we now assume that these equations represent the motion of a test-particle in the flat space,

$$d\sigma^2 = dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2, \tag{17}$$

the time t being regarded as Newtonian, the question naturally arises as to whether the orbit so obtained is invariably plane. As regards the assumption on which the question is based it may be pointed out that the same assumption underlies the usual calculation of the motion of the perihelion of Mercury in general relativity. Without discussing the justification for such an assumption, which is sanctioned by current usage, we only examine whether it leads to plane orbits invariably. The vanishing of the left-hand side of (2) is now equivalent to

$$\begin{vmatrix} \lambda^1 & \lambda^2 & \lambda^3 \\ \dfrac{\delta\lambda^1}{\delta\sigma} & \dfrac{\delta\lambda^2}{\delta\sigma} & \dfrac{\delta\lambda^3}{\delta\sigma} \\ \dfrac{\delta^2\lambda^1}{\delta\sigma^2} & \dfrac{\delta^2\lambda^2}{\delta\sigma^2} & \dfrac{\delta^2\lambda^3}{\delta\sigma^2} \end{vmatrix} = 0, \tag{18}$$

where $\lambda^1, \lambda^2, \lambda^3$ stand for $dr/d\sigma$, $d\theta/d\sigma$, $d\phi/d\sigma$ respectively and $\delta\lambda^i/\delta\sigma$, $\delta^2\lambda^i/\delta\sigma^2$ are the first and second covariant[3] derivatives of λ^i with respect to σ. From the equations of the geodesies we get

$$\ddot{r} - \mathrm{P}\dot{r} + \tfrac{1}{2}\lambda'\dot{r}^2 - re^{-\lambda}(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) + e^{\nu-\lambda}\nu' + \dot{\lambda}\dot{r} = 0, \tag{19}$$

$$\ddot{\theta} - \mathrm{P}\dot{\theta} + \frac{2}{r}\dot{r}\dot{\theta} - \sin\theta\cos\theta\,\dot{\phi}^2 = 0, \tag{20}$$

$$\ddot{\phi} - \mathrm{P}\dot{\phi} + \frac{2}{r}\dot{r}\dot{\phi} + 2\cot\theta\,\dot{\theta}\,\dot{\phi} = 0, \tag{21}$$

where $\mathrm{P} = \tfrac{1}{2}e^{\lambda-\nu}\dot{\lambda}\dot{r}^2 + \nu'\dot{r} + \tfrac{1}{2}\dot{\nu}$, (22)

it being understood that $\lambda' = \partial\lambda/\partial r$, $\dot{\lambda} = \partial\lambda/\partial t$ here. Thus we find

$$\lambda^1 = \dot{r}/\dot{\sigma}, \quad \lambda^2 = \theta\,\dot{\theta}/\dot{\sigma}, \quad \lambda^3 = \dot{\phi}/\dot{\sigma}; \tag{23}$$

$$\frac{\delta\lambda^1}{\delta\sigma} = \frac{d^2r}{d\sigma^2} - r\left(\frac{d\theta}{d\sigma}\right)^2 - r\sin^2\theta\left(\frac{d\phi}{d\sigma}\right)^2 \tag{24}$$

$$= \mathrm{Q} + \mathrm{R}\dot{r}, \tag{25}$$

where

$$\mathrm{Q} = \frac{1}{\dot{\sigma}^2}\left[-\tfrac{1}{2}\lambda' \dot{r}^2 + r(e^{-\lambda} - 1)(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) + e^{\nu-\lambda}\nu' + \dot{\lambda}\dot{r}\right] \tag{26}$$

$$\mathrm{R} = \mathrm{P} - \ddot{\sigma}/\dot{\sigma}^3. \tag{27}$$

In obtaining (25) the independent variable is changed from σ to t and (19) is used. Similarly on using (20) and (21) one obtains

$$\frac{\delta\lambda^2}{\delta\sigma} = \mathrm{R}\,\dot{\theta}, \quad \frac{\delta\lambda^3}{\delta\sigma} = \mathrm{R}\,\dot{\phi}. \tag{28}$$

When (23), (25) and (28) are used in (18) we find that the condition for plane orbits reduces to

$$\frac{\mathrm{Q}}{\dot{\sigma}}\begin{vmatrix} \dot{\theta} & \dot{\phi} \\ \dfrac{\delta^2\lambda^2}{\delta\sigma^2} & \dfrac{\delta^2\lambda^3}{\delta\sigma^2} \end{vmatrix} = 0, \tag{29}$$

Calculations show that

$$\frac{\delta^2\lambda^2}{\delta\sigma^2} = \mathrm{S}\,\dot{\theta}, \quad \frac{\delta^2\lambda^3}{\delta\sigma^2} = \mathrm{S}\,\dot{\phi} \tag{30}$$

where

$$\mathrm{S} = \frac{1}{\dot{\sigma}}\left[\mathrm{PR} + \frac{1}{r}\mathrm{Q} + \dot{\mathrm{R}}\right]. \tag{31}$$

Thus (29) is identically satisfied and all the orbits are invariably plane.

3. We have tried to extend the above analysis to the similar question arising out of the most general line-element,

$$ds^2 = g_{\mu\nu}\,dx^\mu\,dx^\nu. \tag{32}$$

The three equations of motion[4] with $x^4 \equiv t$ as the independent variable are

$$\ddot{x}^i + \Gamma^i_{\alpha\beta}\,\dot{x}^\alpha\,x\beta - \dot{x}^i\,\Gamma^4_{\alpha\beta}\,\dot{x}^\alpha\,\dot{x}\beta = 0, \; i = 1, 2, 3 \tag{33}$$

in the notation of general relativity. Here x^4 means 1. These equations of motion may be considered, as was once suggested by Rosen,[5] with reference to any Euclidean (three-dimensional) metric,

$$d\sigma^2 = h_{ij}\,dx^i\,dx^j.$$

The condition for plane orbits turns out to be extremely complicated, and as no particular cases of interest arise we do not report here our formal result. The case treated in the second section covers the usual gravitational

questions of interest in general relativity, including that of Schwarzschild's external solution. None of the investigators responsible for discussing the motion of the perihelion of Mercury seems to have been aware that once the relativist commits himself to the use of Riemannian co-ordinates the orbit of a test-particle, or of a small planet like Mercury, can be plane only in a special artificial sense. It is in the light of this special sense that we have carried out the discussion of plane orbits in relativity fields.

SUMMARY

We have discovered the most general classical field of force for which the orbit of a test-particle is invariably plane. If the relativistic equations of a test-particle are interpreted in the classical sense, a general result is obtained, of which a particular case accounts for the orbit of Mercury being plane even according to relativists.

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CONSTITUTION OF POPULNIN

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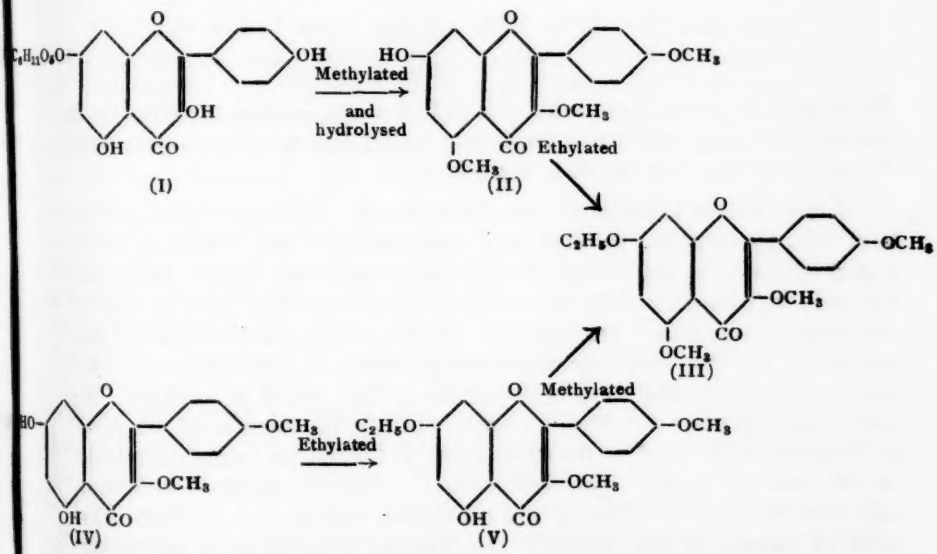
Received September 26, 1946

The glucoside, Populnin,[1] was obtained as the main crystalline component of the flower petals of *Thespesia populnea* and from its composition it was considered to be a monoglucoside of a tetrahydroxy-flavone which was named populnetin. This has now been confirmed by the yield of glucose produced by acid hydrolysis. Populnetin exhibited considerable stability to cold 50% potash and air. As a matter of fact this property was used for its purification. It was therefore considered to be a flavone and not a flavonol. This is now found to be incorrect. Comparison of populnetin and its derivatives with synthetic samples of scutellarein[2] and 5:7:8:4-tetrahydroxy flavone[3] and their derivatives has shown that it is not one of them. The fission of the tetramethyl ether with alcoholic potash yields anisic acid and methoxy fisetol-dimethyl ether establishing definitely that populnetin is a flavonol and should be identical with kaempferol. The identity has been confirmed by comparison with authentic samples, synthetic as well as natural, of kaempferol and its derivatives. It is therefore clear that the criterion of differentiation between flavones and flavonols based on stability to cold alkali and air is not reliable.

It follows from the above results that populnin is a monoglucoside of kæmpferol. In order to locate the position of the sugar group it was methylated by means of dimethyl sulphate and potassium carbonate in anhydrous acetone medium. The product, when hydrolysed with mineral acid, yielded a compound melting at 283–85°. It was a trimethyl ether and did not give any prominent reaction with alcoholic ferric chloride. These properties indicated that the free hydroxyl was not in the 3 or 5 position. The melting points of the corresponding 4′-hydroxy and 7-hydroxy compounds as recorded in the literature are nearly the same as above. But a mixture of the degradation product with the 4′-hydroxy compound recently synthesised in this laboratory[4] melted lower and indefinitely. By elimination it should therefore be concluded that the partial methyl ether obtained from populnin has the hydroxyl group in the 7-position (II) which also indicates the position of the sugar group (I).

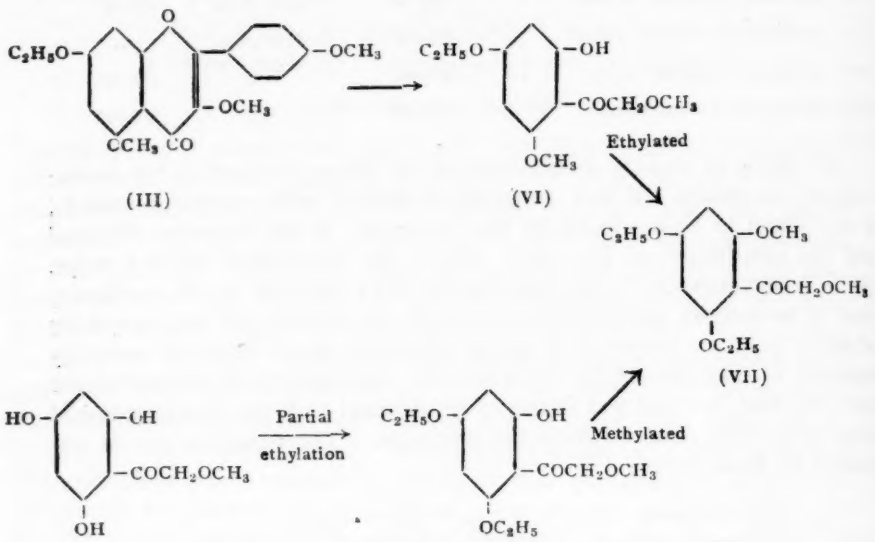
Name of the partial methyl ether	Melting point of hydroxy compound	Ferric chloride reaction	M.P. of acetate
5:7:4′-trimethoxy-3-hydroxy flavone[5] ..	151–52°	Violet brown	190–91°
3:7.4′-trimethoxy-5-hydroxy flavone[6] ..	152–53°	Olive green	..
3:5:4′-trimethoxy-7-hydroxy flavone ..	282–85°	Nil	159–60°
3:5:7-trimethoxy-4′-hydroxy flavone ..	278–80°	Nil	147–49°

In efforts to provide confirmation of the above constitution the mono-hydroxy compound (II) was subjected to fission with alcoholic potash; it was found to be unaffected by this treatment. It was therefore ethylated and the constitution of the ethyl ether (III) established in two ways. (1) 5:7-Dihydroxy-3:4′-dimethoxy-flavone (IV) obtained by the condensation of ω-methoxy phloracetophenone and the sodium salt and anhydride of anisic acid, was subjected to partial ethylation which should be normally expected to take place in the 7-position (V). Subsequently it was methylated and the final product was found to be identical with the abovementioned ethyl ether (III) obtained from the glucoside. The reactions can be explained as given below.



(2) The second method of confirmation involved fission of the ethyl ether (III) whereby anisic acid and a dimethyl-monoethyl phloraceto

phenone (VI) were obtained. Further ethylation of the ketonic product yielded a diethyl ether (VII) whose constitution was again established by synthesis as given below starting from ω-methoxy phloracetophenone.



The formation of the 2:4-diethyl ether (VII) as the degradation product is possible only if in (III) the ethoxyl were in the 7-position, thus confirming that populnin is a 7-glucoside of kæmpferol (I).

A glycoside of kæmpferol with a disaccharose unit in the 7-position has been recently described by Nakamura and Hukuti.[7] The 7-hydroxy compound obtained as the result of methylation and subsequent hydrolysis agrees in its properties with the compound described here in the course of the study of populnin. The Japanese authors report the synthesis of this compound starting from the monomethyl ether of phloroglucinol. But they record the melting point of the acetate as 205° which is too high. We get its melting point as 159–60°. More recently the abstract of the paper of Zemplen and Bognar[8] on the constitution of robinin has become available. As the result of enzymic hydrolysis robinin yielded kæmpferol-7-l-rhamnoside from which by methylation and subsequent hydrolysis 3:5:4′-trimethyl ether of kæmpferol was obtained. Its melting point is given as 288-89° and that of its acetate as 157–58°. These melting points agree with ours closely.

Experimental

Hydrolysis of Populnin.—Populnin (2 g.) was boiled under reflux with 7% sulphuric acid (200 c.c.) for two hours. In about half an hour the glucoside was completely dissolved and the aglucone began to separate out within an hour. The contents were filtered and the filtrate extracted with ether so as to render it free from aglucone. It was then neutralised with sodium carbonate, clarified with neutral lead acetate and the sugar formed was quantitatively estimated by the method of Munson and Walker (Found: glucose, 40·2; $C_{21}H_{20}O_{11}$, H_2O requires glucose, 38·6%). The aglucone was crystallised from aqueous alcohol when it was obtained as fine needles, yellow in colour and melting at 275–76° (Found in sample dried at 120°: C, 63·3; H, 3·9; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%). Mixed melting points of populnetin with both synthetic and natural samples of kæmpferol were undepressed. Populnetin Acetate was prepared by boiling populnetin with acetic anhydride and a few drops of pyridine for two hours. The product was finally recrystallised from ethyl acetate when it came out as colourless short rectangular plates. When heated, the substance sintered strongly and became glassy at about 120° and melted down at 180°, a behaviour characteristic of kæmpferol acetate.

Populnetin Methyl Ether.—As the older method of methylation using sodium hydroxide and dimethyl sulphate was found to be not productive of good yields, the following method was adopted. Populnetin (2 g.) was dissolved in anhydrous acetone (50 c.c.); the solution was treated with anhydrous potassium carbonate (25 g.) and dimethyl sulphate (8 c.c.) and the mixture boiled under reflux for 30 hours. A further quantity of dimethyl sulphate (4 c.c.) was added in small quantities during the first 24 hours. The mixture was finally filtered under suction while still hot and the residue was washed with a small quantity of hot anhydrous acetone. The filtrate was concentrated and on the addition of excess of water a bulky precipitate of the methyl ether was produced. It was filtered and recrystallised from alcohol when it came out as long rectangular plates melting at 165–66° (Found: C, 60·5; H, 6·1; OCH_3, 32·4; and loss on drying at 120° *in vacuo* for 2 hours, 9·2; $C_{19}H_{18}O_6$, $2H_2O$ requires C, 60·3; H, 5·8; OCH_3, 32·8 and loss on drying 9·5%). The substance did not dissolve in alkali and gave no colour with ferric chloride. With concentrated sulphuric acid it gave a yellow solution with weak green fluorescence. The mixed melting point of tetramethyl populnetin with a synthetic sample of tetramethyl kæmpferol (m.p. 165–66°), obtained by methylating 5: 7-dihydroxy-3: 4′-dimethoxy flavone, was undepressed. The above partially methylated flavone was

prepared by condensing ω-methoxy-phloracetophenone with anisic anhydride and sodium anisate according to the method of Robinson and Shinoda.[9]

Decomposition of Populnetin Methyl Ether.—(*a*) 50% *Aqueous potash*: O-Tetramethyl populnetin (0·5 g.) was boiled under reflux in a silver flask with 20 c.c. of 50% aqueous potash for 8 hours. The product was then diluted and acidified with concentrated hydrochloric acid when a colourless solid separated out. The contents were ether-extracted and the ether solution was washed repeatedly with 5% sodium bicarbonate solution till no more acid could be extracted. The bicarbonate extract was acidified and the acid that precipitated out was filtered and recrystallised from alcohol. It was found to be identical with anisic acid. The remaining ether solution contained the ketonic part but the yield of the ketone was not sufficient for identification. Hence the following method of decomposition was employed.

(*b*) *Absolute alcoholic potash.*—O-Tetramethyl populnetin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c.; 8%) for a period of six hours. At the end of the experiment, as much of alcohol as possible was removed by distillation and the residue was dissolved in water. The solution was then filtered free from any suspended insoluble impurities and the clear filtrate was acidified with dilute sulphuric acid. The contents were then ether-extracted and the ether solution was repeatedly washed with 5% sodium bicarbonate solution till no more acid could be extracted. The solvent was then distilled off and the solid obtained was recrystallised from alcohol. It appeared as irregular plates melting at 104–6° and was found to be identical with methoxy fisetol dimethyl ether by a mixed melting point determination with a synthetic sample obtained by partial methylation of ω-methoxy-phloracetophenone.[10]

The sodium bicarbonate extract was acidified and the acid that precipitated out was filtered and recrystallised from alcohol. It was found to be identical with anisic acid.

Methylation of Populnin and Hydrolysis.—Populnin (2 g.) was suspended in anhydrous acetone (50 c.c.) and the contents were refluxed for 30 hours after adding dimethyl sulphate (10 c.c.) and potassium carbonate (25 g.). The mixture was finally filtered under suction while still hot and the residue was washed with a small quantity of hot anhydrous acetone. The filtrate was concentrated and finally as much of acetone as possible was evaporated off. The residue was a viscous semi-solid and it could not be crystallised even after repeated attempts. Therefore it was hydrolysed by boiling with 200 c.c. of 7% sulphuric acid for 2 hours. A clear solution was first obtained

and an almost colourless bulky solid began to separate out at the end of the first half hour. The product (II) was filtered and was recrystallised using a large quantity of alcohol. It came out as colourless short needles melting at 283–85° (Found: C, 66·1; H, 5·2; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). The substance was soluble in alkali to form a light yellow solution and gave no colour with ferric chloride in alcoholic solution. It was stable to alcoholic potash and could be recovered almost completely even after refluxing with 10% absolute alcoholic potash for 8 hours. The mixed melting point with 4′-hydroxy-3 : 5 : 7-trimethoxyflavone (m.p. 278–80°) was considerably depressed and was not sharp (235–55°). Its acetyl derivative was prepared by boiling with acetic anhydride and a few drops of pyridine. It crystallised from ethyl acetate or acetone in the form of colourless flat needles and narrow rectangular plates melting at 159–60°. Mixed melting point with 4′-acetoxy-3 : 5 : 7-trimethoxy flavone was considerably depressed.

Ethylation of (II).—The partial methyl ether of populnetin (II) (1·0 g.) was dissolved in anhydrous acetone (50 c.c.), ethyl iodide (5 g.) and dry potassium carbonate (15 g.) added and the mixture refluxed for 30 hours. At the end of the experiment, the contents were filtered while hot and the residue was washed with hot anhydrous acetone. The filtrate was concentrated and was kept in an ice-chest after dilution with water. The solid that separated out was filtered and washed with dilute alkali to remove any unethylated compound. The product was first crystallised from alcohol when a brownish crystalline solid melting at 80° was obtained; but a colourless sample could be obtained by crystallising it from ethyl acetate. The compound (III) was finally recrystallised from alcohol from which it slowly separated out as rectangular plates melting at 128–30° (Found: C, 67·5; H, 5·4; $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6%).

Decomposition of the Monoethyl-trimethyl Ether (III).—The ethylated product obtained above (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c.; 8%) for a period of 6 hours. As much of alcohol as possible was then removed by distillation; the residue was dissolved in water and the clear solution was acidified with excess of dilute sulphuric acid. The contents were then ether-extracted. The ether solution was shaken three times with 5% sodium bicarbonate solution to extract the acid part (A).

The Ketonic Part (VI).—The remaining ether solution was then washed with water and on distilling off the solvent the residue was found to be a pale yellow viscous liquid which solidified during the course of a few hours when kept in contact with water in an ice-chest. The ketone was crystallised

from dilute alcohol when it came out as rectangular plates melting at 108–10°. It dissolved in alkali to give a bright yellow solution and gave in alcoholic solution on olive green colour with ferric chloride (Found: C, 59·8; H, 7·0; $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%).

The Acid Part (*A*).—The bicarbonate solution on acidification with concentrated hydrochloric acid gave rise to a precipitate which on recrystallisation from alcohol was found to be identical with anisic acid.

Ethylation of (*VI*).—The ketone (VI) (0·5 g.) was dissolved in anhydrous acetone (25 c.c.) and after the addition of ethyl iodide (2 c.c.) and anhydrous potassium carbonate (5 g.) the mixture was boiled under reflux for 30 hours. The solvent was then distilled off and the residue was treated with water when an insoluble liquid separated out. It was ether-extracted and the ether solution was washed with dilute alkali to remove any unethylated ketone. After washing the ether solution free from alkali and distilling off the ether, a reddish yellow viscous liquid remained behind which could not be solidified and recrystallised even after repeated attempts. It was insoluble in aqueous alkali and an alcoholic solution did not give any colour with ferric chloride. Hence the 2:4-dinitrophenyl-hydrazone derivative was prepared by boiling the ketone with an alcoholic solution of 2:4-dinitrophenylhydrazine. The product was washed with dilute hydrochloric acid and was recrystallised from alcohol when it came out as deep red rhombohedral prisms melting at 198–200° (Found: C, 53·4; H, 5·0; $C_{20}H_{24}O_8N_4$ requires C, 53·6,; H, 5·4%).

7-Ethoxy-5-hydroxy-3 : 4'-dimethoxyflavone (*V*).—5 : 7-Dihydroxy-3 : 4'-dimethoxy flavone (IV) was prepared by condensing ω-methoxyphloracetophenone with anisic anhydride and sodium anisate according to the method of Robinson and Shinoda.[9] The flavone (1 g.) was dissolved in dry acetone (50 c.c), ethyl iodide (0·6 g.) and anhydrous potassium carbonate (10 g.) added and the mixture boiled under reflux for 6 hours. At the end of the experiment, acetone was completely distilled off and the residue was taken up with water and ether extracted. From the ether solution, the partially ethylated flavone was extracted by means of dilute aqueous alkali repeatedly until the extraction was complete. The combined alkali extracts were acidified and the precipitate was filtered and recrystallised from alcohol. The 5-hydroxy compound (V) crystallised out as bright yellow rectangular plates melting at 131–32° (Found: C, 66·8; H, 5·1; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%). An alcoholic solution of the compound gave an olive green colour with ferric chloride.

7-Ethoxy-3 : 5 : 4'-trimethoxy flavone.—5-Hydroxy-7-ethoxy-3 : 4'-dimethoxy flavone (V) (1·0 g.) was dissolved in dry acetone (30 c.c.) treated with anhydrous potassium carbonate (15 g.) and excess of dimethyl sulphate (2 c.c.) and the mixture boiled under reflux for 30 hours. The product was worked up in the same way as mentioned for similar cases. When recrystallised from alcohol it came out as thick rectangular plates melting at 128–30° (Found: C, 67·3; H, 6·0; $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6%). It was identical with compound III obtained by the degradation of populnin and the mixed melting point was undepressed.

2-Hydroxy-4-ethoxy-ω: 6-dimethoxy acetophenone.—7-Ethoxy-3: 5: 4'-trimethoxy flavone (1 g.) was treated with absolute alcoholic potash (2 g. of potash in 30 c.c. of absolute alcohol) and the mixture boiled under reflux on a water-bath for about 6 hours. As much of alcohol as possible was then removed by distillation, the residue dissolved in water and the solution acidified with excess of dilute sulphuric acid. The product was then ether-extracted and the ether solution was washed repeatedly with sodium bicarbonate solution until anisic acid was completely removed. The solvent was then distilled off and the solid obtained was recrystallised from dilute alcohol. The ketone crystallised out as rectangular plates melting at 108–10° (Found: C, 60·1; H, 6·7; $C_{12}H_{16}O_5$ requires C, 60·1; H, 6·7%). The mixed melting point with the ketone (VI) obtained from monoethyl trimethyl populnetin (III) was undepressed.

2: 4-Diethoxy-6-hydroxy-ω-methoxy acetophenone (VIII).—ω-Methoxy-phloracetophenone (1 g.) was dissolved in dry acetone (30 c.c.) and the solution refluxed for about six hours after adding ethyl iodide (1·3 c.c.) and anhydrous potassium carbonate (5 g.). The solvent was then removed by distillation, the residue taken up with water and ether extracted. From the ether extract the partially ethylated ω-methoxy-phloracetophenone was separated by extraction with alkali. The alkali solution was then acidified when an almost colourless substance precipitated out. It was filtered and recrystallised from alcohol when it came out as rectangular plates and prisms melting at 110–12° (Found: C, 61·3; H, 7·1; $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%).

2: 4-Diethoxy-ω: 6-dimethoxy acetophenone.—The above ketone (0·5 g.) was dissolved in acetone (30 c.c.) and methylated by boiling for 30 hours, with dimethyl sulphate (2 c.c.) and anhydrous potassium carbonate (5 g.). The solvent was then removed by distillation and the residue treated with water when an insoluble oily product separated out; it was extracted with ether. The ether solution was washed with dilute alkali to remove any

unmethylated ketone. After washing the ether solution free of alkali the solvent was distilled off; a reddish yellow viscous liquid remained behind and it could not be obtained as a solid even after repeated attempts at crystallisation. Hence the 2:4-dinitrophenylhydrazone was prepared by boiling it with an alcoholic solution of 2:4-dinitrophenylhydrazine. The product was recrystallised from alcohol when it came out as deep red rhombohedral prisms melting at 198–200° (Found: C, 53·4; H, 5·4; $C_{20}H_{24}O_8N_4$ requires C, 53·6; H, 5·4%). The mixed melting point with the dinitrophenylhydrazone of the ethylated ketone (VII) obtained from populnin was undepressed. Mixed melting point with 2:4-dinitrophenylhydrazine itself was depressed.

Summary

Populnin is a monoglucoside of populnetin which is shown to be identical with kæmpferol. By the methylation and the subsequent hydrolysis of the glucoside a trimethyl ether of kæmpferol is obtained. Its colour reactions and properties indicate definitely that the free hydroxyl group is not in the 3- or 5-position. It has been compared with the isomeric 4′-hydroxy compound and found to be different. Thus the degradation product should have the hydroxyl in the 7-position. This is confirmed by ethylation and comparison of the ethyl ether and of its alkali degradation product (ketone) with synthetic samples.

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CHEMICAL EXAMINATION OF PLANT INSECTICIDES

Part III. Chemical Components of *Derris Robusta*

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Received September 26, 1946

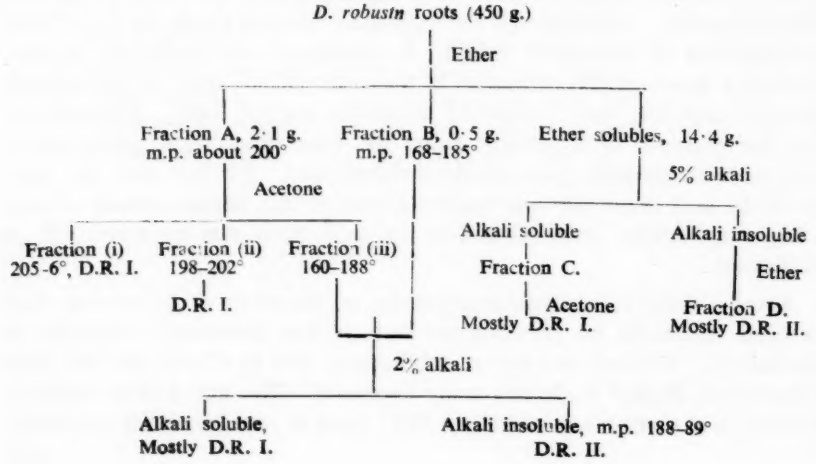
Derris Robusta is very closely related to *D. scandens* botanically as both belong to the same sub-section, Brachypterum of the genus *Derris*. The chief difference is that the former is an erect tree, 30–40 feet high, whereas the latter is a climber. The tree is widely distributed in the tropical areas of the world and occurs in India in the Eastern Himalayas and the Western Peninsula.

Krishna and Ghose[1] examined the roots obtained from Gauhati (Assam) and observed that they did not contain any rotenone. During the course of this examination they isolated from the ether extract a crystalline solid, melting at about 190° and sent it to Rothamsted for toxicity trials; it was found to be non-toxic to *Aphis rumicis* (the bean aphid). Chemical investigation of this sample was conducted by Harper[2] who concluded that it was not a rotenoid, as shown by the Durham test and other reactions, but was a carboxylic acid akin to lonchocarpic acid isolated by Jones.[3] The crystalline substance was named by him ' Robustic acid ' as it was found to possess acidic properties. He proposed the molecular formula $C_{27}H_{24}O_8$ for it from considerations of analytical values. It contained two methoxyl groups; it formed a mono-methyl derivative of the same melting point as the original substance and this was considered to be the methyl ester. Attempts to show the presence of a ketonic group by oximation were unsuccessful. Catalytic hydrogenation gave dihydro-robustic acid. He felt that the titration of the acid in hot alcohol was not a case of true neutralisation, as conflicting results were obtained and as the acid could not be recovered on acidification.

Since a detailed chemical examination of the roots of *D. robusta* had not been conducted by previous workers, it was considered desirable to undertake it. Further, two recent publications, one by Clark[4] and the other by Jones and Haller[5] made this study necessary. The first author reported the isolation of a substance, melting at 190°, from *D. scandens* which resembled

robustic acid. As we were examining the Indian *D. scandens*,[6] we needed a sample of robustic acid for purposes of identification. In the second paper, the authors showed that lonchocarpic acid was not a carboxylic acid as it was originally thought to be. This led us to the expectation that robustic acid also may not be a carboxylic acid and that it may possibly be related to the two substances, scandenin and lonchocarpic acid. In this connection the close botanical relationship between *D. scandens* and *D. robusta* was present in our mind.

The roots of *D. robusta* obtained from Dr. Sri Krishna of the Forest Research Institute, Dehra Dun, were extracted with ether instead of chloroform, as robustic acid was originally isolated by the previous workers from an ether extract. The present sample of the roots gave 3·9% of ether extractives, which were studied on the lines outlined in an earlier publication.[7] The fraction sparingly soluble in ether gave colour reactions similar to those of robustic acid[2] but was found to have a wide melting point range extending up to 200°. Therefore it was fractionated using acetone and as a result of this, a crystalline substance melting sharp at 205–6° was obtained. This was designated as D.R.I. A second crystalline substance (D.R. II) which melted at 188–9° and was insoluble in alkali, was isolated by the alkali treatment of the mixture present in the more soluble portions of the ether extract. This had a crystal structure similar to that of D.R. I and gave similar colour reactions but differed as regards solubility in alkali. Thus the roots of *D. robusta* gave two crystalline components, one melting at 205–6° (major component) and another melting at 188–9°.



Since D.R. I differed from robustic acid as described by Harper in certain of its properties, it was thought desirable to procure a sample of the acid from Dr. Krishna from whom the material used by Dr. Harper was also obtained and effect direct comparison. The crude sample obtained from Dr. Krishna had an indefinite melting point (170–90°) and was therefore purified by crystallisation from acetone. The top fraction melted at 205–6° and was identical with D.R. I. From the other fractions a sample of D.R. II could be obtained. Consequently it could safely be concluded that D.R. I is a purer sample of robustic acid than that employed by Harper for his investigation. It has a higher melting point. There are differences in analytical data as well; ours has given a methoxyl content of 16·2% whereas the methoxyl value recorded by Harper was 13·1%. In carbon percentage also there is a small difference.

Robustic acid can be obtained in a fairly well-developed crystalline form (elongated prisms). Like scandenin, it exhibits a play of colours when viewed at different angles. In solubility also, it closely resembles scandenin and forms a sparingly soluble potassium salt on treatment with aqueous alkali. The substance could be precipitated from the alkali solution either by treatment with mineral acid or by passing carbon dioxide. In the Durham test, it gives a green solution with nitric acid which changes to an unmistakable brilliant red colour on the addition of ammonia. It does not give any phenolic colouration with ferric chloride nor does it respond to the colour reactions of flavonols, resinols or sterols.

Robustic acid contains two methoxyls; from considerations of analytical data and molecular weight determination, the molecular formula $C_{22}H_{26}O_6$ is now assigned to it. Just like scandenin, it could also be titrated with alkali in alcoholic solution and the original substance recovered without any difficulty on acidifying the alkaline solution. Hence the statement of Harper that the substance could not be recovered by acidification after titration with alkali does not seem to be correct. This view is further supported by the observation that robustic acid is quite stable to boiling aqueous alcoholic potash. The minimum molecular weight, 397, calculated from the titration data agrees closely with that obtained by Rast's method. It may be pointed out that Harper's titration values also lead to the same result.

Robustic acid gives a mono-acetate, melting at 196–7° and a mono-methyl ether, melting at 193–4° (*cf.* Harper's m.p. of 'methyl ester' 190°), thereby indicating the presence of one free hydroxyl group. The acetate is insoluble in alkali as is also the methyl ether. As robustic acid can be precipitated from an alkali solution by passing carbon dioxide, as it forms

an acetate which is insoluble in aqueous alkali, and as the methyl derivative does not regenerate robustic acid on treatment with alcoholic potash, it can be said with certainty that the acidic properties of robustic acid are not due to the presence of a carboxylic group as was originally thought but due to a strongly acidic hydroxyl group as in the case of scandenin and lonchocarpic acid. Hence the methyl derivative of robustic acid is a methyl ether and not a methyl ester. In all these properties there is close resemblance between robustic acid, scandenin and lonchocarpic acid. The name robustic acid should still be retained, although the substance is not a carboxylic acid, in order to avoid unnecessary confusion in the literature.

D. R. II has the same crystal structure as D.R. I (robustic acid) and also gives the same colour changes in the Durham test; but it is insoluble in alkali. As it has a lower methoxyl value (17·7%) than the methyl ether of robustic acid (23·2%), it could not be considered to be identical with the latter. From the analytical data, the molecular formula $C_{21}H_{20}O_6$ is assigned to it. Since it appears to be a new substance, it is designated ' Robustenin '.

Experimental

The air-dried roots of medium size (450 g.) obtained from the Forest Research Institute, Dehra Dun, were made into thin shavings and extracted three times with ether at the laboratory temperature soaking each time for 24 hours. The combined extracts (6 litres) were concentrated and the solvent-free residue (17 g.) was taken in a small volume of ether (75 c.c.). The undissolved crystalline material (A) was filtered (2·1 g.). After partial concentration of the filtrate and treatment with methyl alcohol, fraction (B) (0·5 g.) separated and was filtered off.

From the filtrate the solvents were removed under reduced pressure, the residue was taken up in ether and rapidly extracted with 5% aqueous potash. The alkali-soluble portion was liberated by acidification, filtered and washed with boiling petroleum ether to remove fatty matter and was then taken in ethyl alcohol (25 c.c.) and set aside. Next morning a crystalline solid (C) separated and was filtered. By concentration of the solution some more of the same solid was obtained.

The alkali-insoluble ether solution was dried over anhydrous sodium sulphate and the solvent completely removed. The solvent-free residue was taken in a small quantity of carbon tetrachloride (10 c.c.) and set aside. As no solid separated from this, the solvent was distilled under reduced pressure and the residue taken up in ether. The solid (D) that separated was collected.

From the rest of the neutral portion no other crystalline component could be obtained.

Fraction A.—It was colourless and crystalline in appearance. It melted at about 200° (with sintering earlier) and in the Durham test gave a green colour changing to evanescent red, as described by Harper for robustic acid. As its melting point was not quite definite and was higher than that recorded for robustic acid (190°) it was fractionated. Acetone was used for this purpose and the following three fractions were collected:

	Melting point	Crystal structure	Durham test	Ferric chloride colour
Fraction (i) ..	205–6°	Large rectangular prisms	Green to red	Negative
Do (ii) ..	198–202°	do	do	do
Do (iii) .	160– 88°	do	do	do

Fraction (i) appeared to consist of a single entity and the melting point was not raised by further crystallisation. It was therefore marked D.R. I. Fraction (ii) consisted essentially of this and could be purified by further crystallisation whereas fraction (iii) behaved like a mixture.

Fraction B.—The solid had a wide melting point range, 168–85° but gave the colour changes in the Durham test similar to those given by D.R. I. Since fraction (iii) from (A) and this solid had similar melting point ranges, they were combined and treated with 2% aqueous alkali and the mixture heated and filtered. The clear solution was acidified and the product obtained was found to have a melting point of 192–96°. On crystallisation from alcohol the melting point rose and the product was found to be identical with D.R. I.

The alkali-insoluble solid was washed with hot water to remove any potassium salt that might have been present and then crystallised from alcohol. After two crystallisations it had a sharp melting point, 188–9° (mixed melting point with D.R. I. depressed). In the Durham test, the colour change was from dirty green to evanescent red. This substance was marked D.R. II.

Fraction C.—It melted fairly sharp at 189–91° and had the same properties as D.R. I. Recrystallisation raised the melting point to 193° and not further. However the mixture with D.R. I also melted at the same temperature and methylation of the substance yielded a methyl ether identical with that of D.R. I. It was therefore concluded that this fraction consisted

mainly of D.R. I. The cause of the lower melting point will receive further attention when more quantities of this fraction are again obtained.

Fraction D.—Its melting point was indefinite 170–80°, it was insoluble in alkali and gave in the Durham test the same colour changes as D.R. II. The quantity was too small to effect detailed purification.

Purification of the robustic acid sample obtained from Dehra Dun.—The crude sample (2·5 g., m.p. range 170–90°) was taken in boiling acetone (50 c.c.) and the insoluole portion, which was appreciable in amount, was filtered off. The first crop (0·7 g.) melted at 198–202° and appeared as colourless rectangular prisms. The melting point could be raised to 205–6° by another crystallisation and the mixed melting point with D.R. I was undepressed. The second crop (1·3 g.) had an indefinite melting point 170–88°. This on treatment with alkali gave an alkali-insoluble product identical with D.R. II.

D.R. I is hence forward designated robustic acid.

Robustic acid.—On slow crystallisation, it could be obtained in a fairly well-developed form and appeared as elongated prisms under the microscope. It was readily soluble in chloroform, boiling acetone and alcohol and less soluble in petroleum ether and benzene. It had greater solubility than scandenin in ether. Though it was insoluble in water, it was found to be soluble in warm aqueous potash from which the sparingly soluble potassium salt separated on cooling. On acidification of the alkali solution, the substance was reprecipitated.

Robustic acid dissolved in concentrated sulphuric acid forming an intense red solution without any visible fluorescence. In the Durham test it did not give the rotenoid colour changes but gave a green colour changing to brilliant red. This red colour was unmistakable and could not be missed. The compound did not respond to the sterol or resinol colour reactions. When a speck of the substance was treated with gallic acid and concentrated sulphuric acid and gently heated, no blue colour was produced, thereby indicating the absence of methylene-dioxy grouping in the molecule [Found: C, 69·2; H, 5·2; OCH_3, 16·2%. Mol. weight (Rast) 404, $C_{22}H_{20}O_6$ requires C, 69·5; H, 5·3; 2–OCH_3, 16·4% Mol. weight 380. *Cf.* Harper's values C, 68·4; H, 5·1; OCH_3, 13·1%. Mol. weight (Rast) 496, 451].

Micro-titration.—The substance was dissolved in hot neutralised alcohol and titrated with standard alkali using phenolphthalein as the indicator. The end point was sharp (61·0 mg. of the substance required 4·65 c.c. of 0·033 N alkali. Mol. weight 397. Harper's values: 53·65 mg. required

7·05 c.c. of 0·02 N. NaOH; Mol. weight 380). The substance was recovered on acidification and dilution with water.

Mono-acetate.—The acetate was prepared by boiling the substance with acetic anhydride and sodium acetate. The product crystallised from ethyl acetate as rectangular rods and prisms melting at 196-7°; the mixed melting point with the original substance was depressed (Found: C, 68·1; H, 5·3; $C_{24}H_{22}O_6$ requires C, 68·2; H, 5·3%).

The acetate was found to be insoluble in 5% aqueous alkali even after warming the solution, thereby indicating the absence of a carboxylic group in the substance.

Mono-methyl ether.—The methylation was carried out in anhydrous acetone medium using dimethyl sulphate and potassium carbonate. On concentration of the acetone solution to a small volume, a crystalline solid, melting at 192–3°, was obtained; the mixed melting point with the original substance was considerably depressed. It was insoluble in aqueous alkali and did not yield robustic acid on treatment with alcoholic potash. The methyl ether was recrystallised from alcohol when it came out as prismatic needles melting at 193–4° (Found: OCH_3, 23·2%. $C_{23}H_{22}O_6$ requires 3-OCH_3, 23·6%).

D.R. II (*Robustenin*).—It appeared as rectangular prisms under the microscope and gave in the Durham test a dirty green colour changing to evanescent red. With ferric chloride, no colouration was obtained [Found: C, 68·5; H, 5·7; OCH_3, 17·7%. Molecular weight (Rast) 390; $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·4; (2) OCH_3, 16·9%; Molecular weight, 368]. As it appeared to be a new substance, it was designated 'robustenin'.

Our thanks are due to Dr. Sri Krishna of the Forest Research Institute, Dehra Dun for the supply of samples of the roots of *D. robusta* and also of a sample of the crystalline component of these roots.

Summary

A detailed examination of *D. robusta* has now been made and two crystalline components isolated. The main component (D.R. I) melts at 205–6° and agrees, in general, with the properties of robustic acid described by Harper except in melting point and analytical values. The same substance (D.R. I) was also obtained from the crude sample of robustic acid supplied by the Forest Research Institute, Dehra Dun, from where Dr. Harper also got his material. The name robustic acid has been retained for it. The molecular formula, $C_{22}H_{20}O_6$ agrees with the results more closely. The molecule contains two methoxyls and one hydroxyl group. The acid nature

of robustic acid has now been shown to be due to a phenolic hydroxyl just as in the case of scandenin and lonchocarpic acid. These three compounds seem to form a new type not having any simple relationship with rotenone.

The second component now named 'robustenin' melts at 188–89°, is neutral in nature and has the probable molecular formula $C_{21}H_{20}O_6$. It contains two methoxyls.

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1152-46 Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences.